THE PREPARATION AND ANALYSIS OF ORGANIC COMPOUNDS

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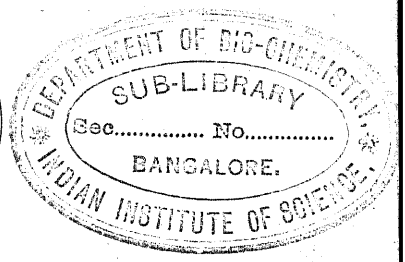
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WITH 42 ILLUSTRATIONS





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PREFACE

In this volume the authors have endeavoured to place before the student a comprehensive course of practical organic chemistry.

This course includes typical processes of chemical syntheses, as well as the general methods of organic analysis, both qualitative and quantitative.

In **Section I.** details of the general processes of organic manipulation are described, and experiments are given which may be carried out by the student who is commencing the study of the subject.

Section II. contains a comprehensive series of preparations. The authors have endeavoured to keep the following points in mind:

(*a*) That the experiments are described in such detail that the average student will have no difficulty in carrying out the work without the necessity of constant supervision.

(*b*) That since it is very unsatisfactory that any student should carry out an organic preparation without first fully understanding the theoretical processes involved, in every case the preparation is prefaced by a full explanation of the reactions involved, and each sub-section by an account of the methods applicable for the synthesis of the class of compound under consideration.

The preparations have been arranged in families of related compounds so that the student may be made familiar with the general processes of chemical synthesis. This method has been adopted in place of the somewhat disconnected series that would result if the preparations were arranged merely in order of increasing difficulty. For this purpose processes of general application have been selected, and it is believed that the book itself will thus be a valuable addition to the theoretical, as well as the practical, library of the organic chemist.

Section III. is devoted to the qualitative identification of organic compounds. In this section a serious endeavour has been made to systematise organic analysis, and to adopt the orderly arrangement that is so familiar in inorganic chemistry. For this purpose a definite scheme of analysis, a considerable part of which is original in conception, is set out, and this section includes some fifteen tables of analysis, by means of which the substance is placed

definitely in a particular sub-group. Detailed tables of the characteristic properties of the more common organic compounds are also given in order to identify definitely the individual substance. These detailed tables, some thirty-seven in number, give the principal characteristics of about 650 compounds.

In addition the separation of mixtures of organic compounds is described, and three tables of analytical separation are given.

In **Section IV.** the more usual processes of ultimate analysis are given in detail.

Section V. The methods of the determination of molecular weights and the estimation of typical groups are described. In this section processes for the determination of the relative amounts of ortho-, meta- and para-isomers in a mixture are outlined.

It is anticipated that in addition to the course giving an insight into modern organic chemistry, it will be fully sufficient to meet the requirements of the Honours Examinations of the Universities, the Examination of the Institute of Chemistry, and of other similar bodies.

The authors desire to express their indebtedness to Dr. J. C. Crocker, M.A., F.I.C., Dr. F. Matthews, F.I.C., and to Mr. F. W. Hodges, M.Sc., for many valuable suggestions, and to Mr. George Arnall, F.S.I., for special help in connection with the diagrams.

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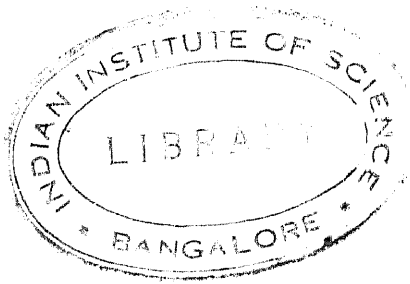
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ABBREVIATIONS

M.P.	melting-point.
B.P.	boiling-point.
S.P.	setting-point.
a.	above, used in connection with melting-points and boiling-points.
d.	decomposes, used in connection with melting-points and boiling-points.
Δ	density.
gm.	gram.
dil.	dilute.
conc.	concentrated.
s.	soluble.
e.s.	easily soluble.
m.s.	moderately soluble.
s.s.	sparingly soluble.
v.s.	very soluble.
v.s.s.	very sparingly soluble.
i.s.	insoluble.
pptte.	precipitate.
$[\alpha]_D$.	specific rotation.
m-	meta.
o-	ortho.
p-	para.
d-	dextro.
l-	lævo.
i-	inactive.
n-	normal.

ABBREVIATIONS USED IN CONNECTION WITH COLOUR REACTIONS.

B.	blue.
G.	green.
O.	orange.
R.	red.
V.	violet.
Y.	yellow.

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SECTION I

CRYSTALLISATION, FILTRATION, SUBLIMATION AND DISTILLATION. MELTING-POINT, SETTING-POINT, BOILING-POINT, DENSITY OF LIQUIDS AND SOLIDS, REFRACTIVE INDEX AND OPTICAL ROTATION.

1. Introductory Remarks.—In connection with the investigation of the properties of organic substances it is frequently necessary to ascertain the absolute purity of the compounds used. For this purpose it may be necessary to carry out an exhaustive series of physical determinations, as well as a complete ultimate analysis of the substance. In practice, however, its appearance, if crystalline, the sharpness of its melting-point and the constancy of the boiling-point are valuable indications of purity. In no case should an identification be attempted or a preparation be considered finished, unless the purity of the compound has been tested by judicious examination. The more usual operations employed for the purification of organic substances, crystallisation, filtration, sublimation and distillation, are described in this section. These descriptions are followed by an account of the methods used for determining the melting-point and setting-point of an easily fusible solid, the boiling-point of a liquid and the density of a liquid and of a solid. Brief notes are also given on refractive index and optical activity.

CRYSTALLISATION AND FILTRATION

2. For the process of crystallisation it is first necessary to select, by experiment, a suitable solvent for crystallisation. The substance should not be too soluble in the cold solvent. The more usual solvents for organic compounds are: (i.) water, (ii.) alcohol, (iii.) glacial acetic acid, and (iv.) acetone. Less common solvents are (v.) ether, (vi.) petroleum ether (ligroin), and (vii.) benzene. Mixtures of two solvents are also used, such as (viii.) water and alcohol, and (ix.) water and acetic acid. If a solution of the substance has been made in hot alcohol it is usually advantageous

to add hot water (80° C.) until turbidity appears, and then leave the solution to crystallise.

The usual procedure is to powder the substance roughly and treat it with just insufficient of the hot solvent for complete solution. The addition of a very small quantity of good *animal charcoal* during the process of solution is usually made to decolorise and clarify the solution by absorbing the tarry products formed. If the compound under experiment has a melting-point below the temperature of the boiling solvent, then the saturated solution is made at a temperature not more than five degrees above the temperature at which the compound melts; as otherwise, on cooling, the product will separate out as an oil and will ultimately solidify into a solid mass.

The saturated solution thus obtained should be filtered quickly,

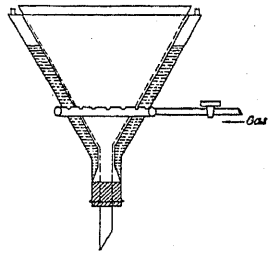


FIG. 1.—Hot-water Funnel.

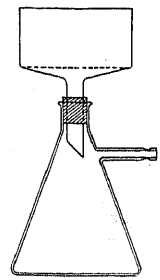


FIG. 2.—Buchner Funnel and Flask.

whilst it is hot. This may be done by employing a hot filter, in which the glass funnel is fitted with a hot-water jacket (Fig. 1), but usually it is better and more expeditious to use a suction flask and Buchner funnel (Fig. 2), the perforated portion of the latter covered with filter paper cut to size. The funnel and flask should both be warmed with hot water before filtering. In place of a Buchner funnel, an ordinary glass funnel holding a perforated porcelain disc may be substituted, but the filtering surface is not so great in this case, and consequently the time of filtration is increased.

Caution.—Before filtering inflammable solvents through hot-water funnels the heating flame must be turned out.

3. Crystallisation by cooling is then carried out in a beaker covered with a clock glass. The latter is used to diminish evaporation at the surface and prevent the formation of an impure product. It is frequently found that organic solutions *supercool.* In such

cases crystallisation may be promoted by scratching the sides of the containing vessel with a sharp glass rod or by the introduction of a very small quantity of the solid substance.

4. Drying the Crystals.—The crystallised product is freed as far as possible from adherent mother-liquor by filtration, using a Buchner funnel and suction flask (Fig. 2), afterwards washing the solid with a small quantity of the pure solvent. For larger masses the crystals should be separated from the mother-liquor by means of a centrifuge. The crystals are then pressed on to an unglazed plate and left to dry, or the crystals may be squeezed between layers of filter paper, and subsequently dried in a vacuum desiccator. The steam oven may also be used for drying, provided that the substance does not melt, or decompose below 100° C.

EXPERIMENT 1.—Purify by crystallisation two of the following substances: (*a*) salicylic acid from water, (*b*) *m*-dinitrobenzene from aqueous alcohol (1 volume methylated spirit to 1 volume water), (*c*) para-nitroacetanilide from alcohol (methylated spirit) (*d*) para-nitrosodimethylaniline from ether.

SUBLIMATION

5. The process of purification by sublimation is much less usual than that by crystallisation, since comparatively few substances pass directly from the solid to the gaseous phase without the intermediate formation of a liquid. Such compounds as iodine, iodoform, and anthraquinone are purified in this way. The crude dry product is placed in an evaporating dish supported on a sand bath. The dish is covered with a piece of asbestos sheet with a hole in the centre, and surmounted with a glass funnel as shown in Fig. 3.

The dish is gently heated, when the vapours which pass through the perforation in the asbestos will crystallise on coming in contact with the cool glass, and any crystals that fall will collect on the sheet of asbestos. Unless the surface is known to be perfectly dry the first portion of the vapour should be allowed to escape.

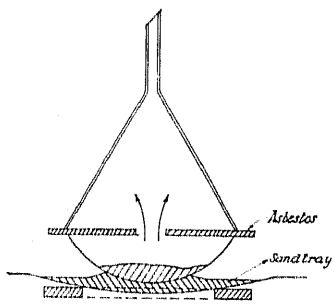


FIG. 3.—Sublimation on a Small Scale.

EXPERIMENT 2.—Purify 5 gm. of anthraquinone by sublimation by the method described above.

Purification by sublimation on a larger scale is best accomplished by the following method applicable to compounds, such as β-naphthol, that first melt and then sublime. The naphthol is melted in a tubulured retort with a shortened neck, as shown in Fig. 4.

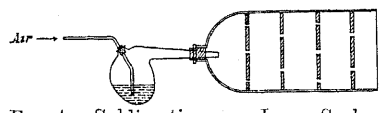


FIG. 4.—Sublimation on a Large Scale.

Air is gently blown in and the naphthol vapour is carried over into a "Winchester quart" bottle, the bottom of which has been cut out. The bottle is partitioned off with a number of cardboard or asbestos discs freely perforated so as to form baffle plates.

DISTILLATION

Distillation is the most general method of purifying organic substances.

6. Simple Distillation.—In this operation the substance is gently boiled in a distilling flask, fitted with a thermometer, and attached to a water condenser, as shown below. It is preferable to use good wooden corks rather than rubber bungs, the latter being so readily attacked by many organic compounds. When volatile and inflammable liquids are distilled they should be heated by means of a water or oil-bath, and the condensate should pass through an adapter directly into the cooled receiver. A few small pieces of

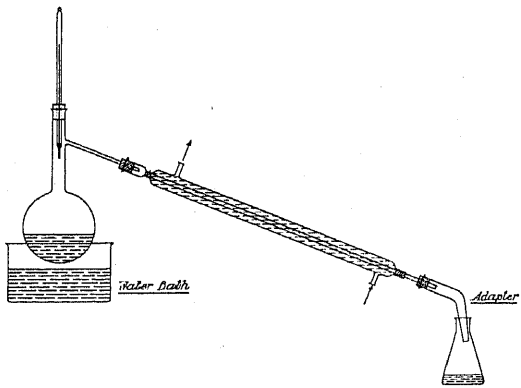


FIG. 5.—Simple Distillation of Easily Volatile Compounds.

unglazed earthenware (porous pot) should be placed in the distilling flask to diminish bumping. The apparatus should be arranged as shown in Fig. 5.

For liquids that boil above 100° C. an air condenser, consisting of a plain glass tube 30 in. long, should replace the water condenser. See Fig. 6.

7. Fractional distillation is employed for the separation of mixtures of two or more miscible liquids. In this case a round-bottomed flask, fitted with a fractionating column (Fig. 7) replaces the ordinary distillation flask. The weight or volume of each fraction and the temperature at which it distils is noted. The liquid will begin to boil at about the boiling-point of the more volatile liquid, but as the heating is continued the boiling-point will gradually rise. After a time the boiling-point will rise rapidly until it approaches the boiling-point of the less volatile liquid,

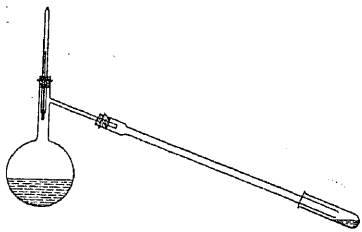


FIG. 6.—Distillation, using an Air Condenser.

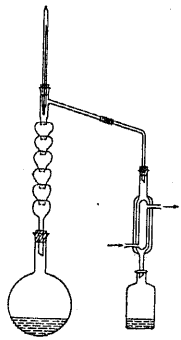


FIG. 7.—Fractional Distillation.

when it will again rise slowly until the whole of the liquid has distilled.

If the volume of the distillate is measured from time to time, it will be found that the two largest volumes have been obtained while the thermometer indicates approximately the boiling-points of the two liquid constituents of the mixture. If the separate fractions of the distillate which come over at fairly constant temperatures have been received in separate vessels, it will be seen that a partial separation of the constituents has been effected. The two main "fractions" may be now separately distilled or "refractionated," and separated in a similar manner into fractions; when a fairly pure sample of each of the constituent liquids may be obtained by collecting separately those fractions which distil over near the boiling-points of the respective constituents. By a further "refractionation," a pure specimen of each of the original liquids may ultimately be obtained.

Several types of fractionating columns are shown in Fig. 8.

EXPERIMENT 3.—**Purification of Alcohol.**—Fractionally distil 200 c.c. of methylated spirits, collecting the following fractions: (*a*) up to 75° C., (*b*) from 75°–80° C., (*c*) above 80° C. Carefully refractionate the middle fraction, from 78°–79° C., to obtain a specimen of pure ethyl alcohol. Ethyl alcohol is miscible with water in all proportions. B.P. 78·5° C. $\Delta = 0{\cdot}793$ at 15° C.

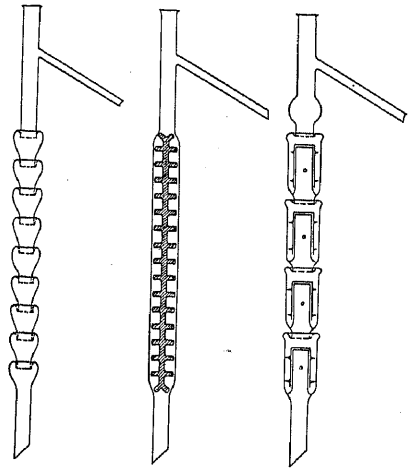


FIG. 8.—Types of Fractionating Columns.

8. Distillation in Steam.—Many substances, even those boiling far above 100° C., and normally not volatile without decomposition, possess the property of distilling in a current of steam. Steam distillation is thus very frequently employed for the purification or separation of organic compounds.

The apparatus should be arranged as shown in Fig. 9. The can *A* contains water and is connected in the manner shown with the flask *B*, which is attached to a condenser.

It will be noticed that the steam can *A* is provided with a long glass tube passing to the bottom. This acts as a safety tube. The round-bottomed flask *B* is inclined at an angle so that the amount of liquid carried over mechanically by bumping is lessened. When a rapid current of steam is passed into *B*, the latter need not also be heated directly with a burner, unless the bulk of liquid in *B* becomes too large.

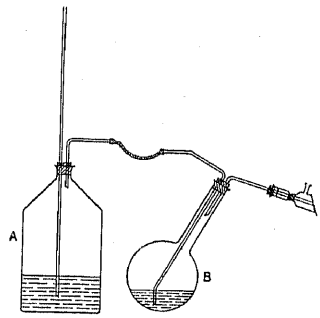


FIG. 9.—Steam Distillation.

EXPERIMENT 4.—**Purification of Aniline. $C_6H_5NH_2$.**—Place 50 gm. of commercial aniline in the flask *B* and pass steam in until the condensate is free from oily drops. Separate the aniline from the aqueous distillate by placing it in a separating funnel (Fig. 10) and tapping off the lower layer.

Leave it to stand for some hours over a few pieces of solid caustic potash. Pour off into a distilling flask and distil, using an air condenser. Collect the distillate from 182°–184° C. Aniline is a pale-coloured oil. B.P. 184° C. $\Delta = 1{\cdot}026$.

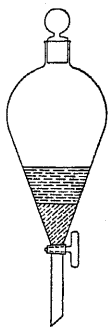


FIG. 10.—Separating Funnel.

EXPERIMENT 5.—**Separation of Nitrobenzene and Aniline.**—To about 50 gm. of a mixture of equal parts of aniline and nitrobenzene add 100 c.c. of water and 75 c.c. of concentrated hydrochloric acid and steam distil as described above. When no more nitrobenzene distils over, add a strong solution of caustic soda to the liquid left until distinctly alkaline and again steam distil to obtain the aniline. Purify each product in the manner described in Experiment 4. Nitrobenzene, $C_6H_5NO_2$, is a pale-coloured oil. B.P. = 207° C. $\Delta = 1{\cdot}208$.

9. Principle of Steam Distillation.—In the case of two non-miscible liquids the observed vapour pressure at any temperature is equal to the sum of the vapour pressures of the two liquids when heated separately. The liquids therefore evaporate independently of each other and obey Dalton's law of partial pressures. The rapidity with which a substance distils with steam depends therefore both on its vapour density and on its vapour pressure relative to water. Under normal conditions a mixture of nitrobenzene and water distils at 99° C., at which temperature the vapour pressure of water is 733 mm., and hence that of nitrobenzene is 27 mm. Thus, of the total volume of vapour $\frac{733}{760}$ will be steam, and $\frac{27}{760}$ will be nitrobenzene, and the relative weights will be as

$$\frac{733 \times 9}{760} : \frac{27 \times 60{\cdot}5}{760} \quad i.e., \ 4{\cdot}05 : 1$$

V.D. of water = 9, of nitrobenzene = 60·5), or in other words 19 per cent. by weight of the distillate is nitrobenzene, and this ratio continues until either the water or the nitrobenzene is exhausted.

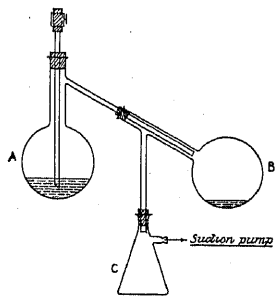


FIG. 11.—Distillation under Reduced Pressure.

10. Distillation under Reduced Pressure. (Distillation in Vacuo.)—Many compounds which volatilise with decomposition at atmospheric pressure may be distilled unchanged under reduced pressure.

The simplest form of apparatus is shown in Fig. 11, the side tube of the principal distillation flask *A* leading into the bulb of the second flask *B*. This is connected to a suction flask *C*, to serve as a trap, and thence to a suction pump. Dip-

ping into the liquid is a piece of fine-bore glass tubing drawn to a fine jet, and at the upper end of which is fixed a short piece of thick-walled rubber tubing almost closed by an adjustable clip. By this means a slow series of air bubbles is drawn through the heated liquid. This procedure minimises bumping and frothing. All bungs must be of sound rubber, neatly bored.

11. Fractional Distillation under Reduced Pressure.—It is sometimes desirable to collect a series of separate fractions. In such a case it is advisable to arrange the vacuum apparatus so that these separate quantities may be removed without alteration of the pressure and without discontinuing the distillation. To accomplish this the apparatus should be arranged as shown in

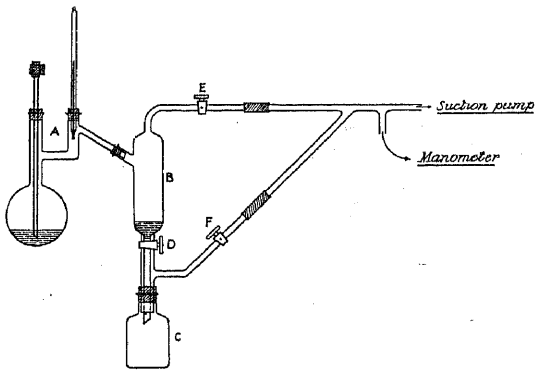


FIG. 12.—Fractional Distillation under Reduced Pressure.

Fig. 12. The distillation flask *A* is provided with a double neck so that the temperature of each fraction may be noted. It is attached to a double receiver *B* and *C*, connected to a manometer and a suction pump. When the desired fraction has been collected in *C*, the two-way taps *D* and *E* are closed, and air is admitted to *C* by means of the three-way tap *F*. The receiver *C* may then be changed, the new receiver evacuated, and the whole process repeated without interrupting the distillation.

DETERMINATION OF THE MELTING-POINT OF A SOLID

The temperature at which an organic substance melts is of importance, not only for identifying a substance, but also as an indication of its purity. A solid substance will usually melt sharply at a particular temperature if it is pure; but if it is

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impure it will usually soften before its melting-point is reached, and there may be a difference of several degrees between the softening-point and the temperature at which it becomes fluid.

Two methods, which are commonly in use for determining the melting-point of a substance, are described below.

12. First Method.—The solid substance is placed in a thin-walled glass tube, which is about 1 mm. in diameter and is sealed at one end. Such a tube is readily made by drawing out a thin-walled narrow test tube in the Bunsen flame. The long tube thus produced is cut into tubes 3 cm. in length, each of which is then closed at one end by fusion in the flame.

The open end of one of these tubes is dipped into the finely powdered substance, and the tube is placed mouth upwards and gently tapped to cause the powder to fall to the closed end. These operations are repeated until about 3 mm. of the tube is filled with the powder.

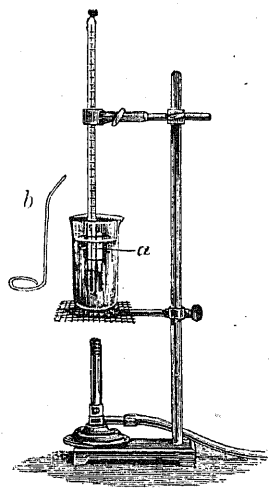


FIG. 13.

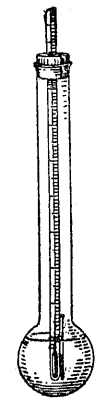


FIG. 14.

Determination of Melting-point.

The tube is then attached closely to the stem of a delicate thermometer so that the powder is alongside the bulb, by means of a little rubber ring, cut off small rubber tubing. The rubber ring must be placed sufficiently high so that it is not immersed in the heating liquid (Fig. 13).

The thermometer and tube are then placed in a beaker containing a liquid which has a higher boiling-point than the melting-point of the solid. Water, strong sulphuric acid, or pure paraffin oil may be used in the beaker, according to the temperature which is required.

The beaker is then heated until the solid melts, and the temperature of liquefaction is accurately noted by the thermometer.

During the process of heating the contents of the beaker should

be constantly mixed by means of a stirrer, which is made of bent glass rod or stout wire in the shape shown at *b* in Fig. 13. This continuous stirring is necessary, in order to secure a uniform temperature throughout the mass of the liquid during the determination.

The process should be repeated several times with fresh portions of the substance, and the mean temperature, which has been obtained from these experiments, should be taken as the melting-point of the solid.

If the mercury thread of the thermometer extends above the surface of the liquid, the correction which is described in the *Note* in paragraph **15** must be applied to the reading.

EXPERIMENT 6.—Determine the melting-point of naphthalene, using a beaker which contains water for the bath. The melting-point should be approximately 80° C.

13. Second Method.—A modified form of vessel for determining melting-points is shown in Fig. 14. It is made by blowing a bulb at the end of a piece of wide glass tube, which should be about 15 cm. in length, with a diameter of about 3 cm., and the bulb should be about 5 cm. in diameter. This bulb is nearly filled with strong sulphuric acid.

The bulb of the thermometer is then wetted with the acid by dipping it beneath the surface (Fig. 14), and the tube containing the substance is placed alongside and in close contact with the wet thermometer bulb as is shown in Fig. 13, *a*; the tube will adhere to the wetted bulb.

The thermometer bulb with the adhering tube is then immersed in the acid, the upper part of the tube remaining above the surface of the liquid; the small tube will continue to adhere to the thermometer owing to the surface tension of the acid film. The stem of the thermometer is held in this position by means of a cork inserted in the mouth of the large tube, the cork having a groove cut in its edge to permit the air to escape as it is expanded by heat.

When the apparatus has been properly adjusted, heat is gradually applied to the bulb, and the melting-point is observed. The process is repeated, and the results obtained are dealt with as has been already described in the first method (**12**).

The discoloration of the acid, which may be caused by its continued use, may be removed by the addition of a crystal of potassium nitrate.

EXPERIMENT 7.—Determine the melting-point of acetanilide or of benzoic acid by the above method.

DETERMINATION OF THE SETTING-POINT OF A SOLID

14. The setting-point or temperature of solidification of a solid is used in certain cases for the identification of an organic solid.

The apparatus employed for this purpose is shown in Fig. 15. The receptacle for holding the solid consists essentially of a double-walled tube, with an air space between, so that the temperature of the melted substance falls regularly and slowly. This tube is placed in a bath of colourless, odourless, high-boiling liquid paraffin. A quantity of the pure compound is introduced into the tube, melted by heating the external bath, and the whole apparatus allowed to cool. During cooling the substance is stirred continuously and the point of solidification read by a thermometer reading to the one-twentieth of a degree. Many substances supercool, but on crystallisation give a steady freezing-point which remains constant until solidification is complete. If a double-walled tube is not available, it may be replaced by two thin-walled glass tubes, connected by a cork, so that an air space is maintained between.

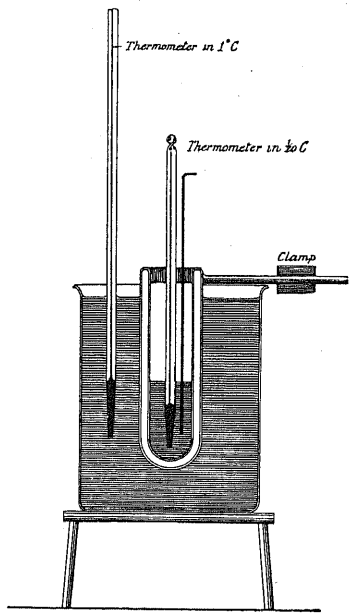


FIG. 15.—Determination of Setting-point.

EXPERIMENT 8.—Determine the setting-point of a specimen of naphthalene or para-toluidine, and compare the value obtained with the melting-point of the compound obtained as described in paragraph **13**.

DETERMINATION OF THE BOILING-POINT OF A LIQUID

The boiling-point of a pure liquid is always the same when the liquid is boiling under the same pressure and similar conditions. This constancy of boiling-point is frequently made use of to ascertain the purity of a liquid, as well as to detect its nature.

Two methods are described for the determination of the boiling-point. In the first the temperature of the vapour of the boiling

liquid is measured, and is the method usually employed. The second method is resorted to when only a small quantity of the liquid is available.

15. First Method.—The liquid is placed in a flask, the neck of which is provided with a delivery tube at the side. The neck is closed by a perforated cork, through which a thermometer passes. The bulb of the thermometer should be fixed just above the surface of the liquid.

Heat is gradually applied until the liquid boils, the side tube serving to carry away the vapour which is produced. The bulb and part of the stem of the thermometer are thus constantly surrounded by the vapour of the boiling liquid.

If the boiling-point of the liquid is below 120° C., a cold-water condenser should be connected with the side tube of the flask, as shown in Fig. 5, page 4. If the boiling-point is above 120°, an air condenser should be used (Fig. 6, page 5).

As soon as the reading of the thermometer remains constant, the temperature is registered as the boiling-point of the liquid.

NOTE.—This reading will, however, require to be corrected if the thread of mercury in the thermometer extends above the cork. The following formula gives the correction to be added :—

$$N(T - t) \times 0{\cdot}000156.$$

Here N is the number of degrees on the thermometer stem which are not heated by the vapour. T is the temperature indicated by the thermometer, t is the temperature taken by placing the bulb of a second thermometer midway between the top of the cork and of the mercury column during the process, this second bulb being screened from the direct heat of the Bunsen flame, and 0·000156 is the apparent coefficient of expansion of mercury.

It should be remembered that any considerable difference in the atmospheric pressure will cause an appreciable variation in the boiling-point. It will therefore be necessary either to arrange a means for adjusting the pressure within the flask, if the atmospheric pressure varies much from 760 mm. of mercury ; or, as an alternative, to specify the barometric pressure read during the time of taking the boiling-point. Thus, if the boiling-point observed is 62° C. and the barometric pressure is 760 mm., it may be entered 62° C. /760 mm.

A rough correction may be applied, if necessary, on the assumption that an increase or a diminution of 20 mm. in the atmospheric pressure from 760 mm. causes approximately an increase or a diminution of 1° C. in the boiling-point.

All the boiling-points given in this book correspond to the normal atmospheric pressure of 760 mm. of mercury.

EXPERIMENT 9.—Determine the boiling-point of chloroform, using a water condenser, and of aniline, using an air condenser.

16. Second Method.—The method described below may be employed when only a small quantity of liquid is available. It gives results which are usually within one degree of the true boiling-point.

About 1 c.c. of the liquid is placed in a thin-walled test tube, which may be about 8 cm. in length and 1 cm. in diameter. The test tube is fastened to the thermometer by means of fine wire, or by thin rubber bands, as is shown in Fig. 16. A fine capillary tube of thin glass, a little more than 8 cm. in length, is then prepared by heating the walls about 1 cm. from one end in the tip of the flame for a second, so as just to fuse them together; and the tube is placed in the test tube as is shown in the figure.

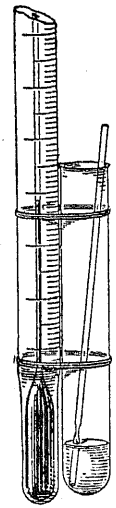


FIG. 16.—Boiling-point Apparatus.

The apparatus is now dipped into a beaker containing sulphuric acid, the mouth of the test tube projecting above the surface of the liquid. When the acid is heated, small bubbles of air will slowly escape from the lower end of the capillary tube. As the temperature gradually rises, the evolution of vapour bubbles will eventually become rapid and continuous, indicating that the liquid has attained its boiling-point. The temperature is then read upon the thermometer. The determination should be confirmed by repeating the process with a fresh capillary tube.

EXPERIMENT 10.—Determine the boiling-point of a sample of benzene by the above method.

DENSITY OF A LIQUID SUBSTANCE

17. The Density of a Liquid is of considerable importance, since it may be used not only for the identification of the liquid, but also for determining its purity and strength, as in the case of aqueous solutions of alcohol (paragraph **504**).

To obtain the density of a liquid the usual procedure is to compare the weight of a volume of the liquid with the weight

of an equal volume of water, the volume in each case being measured at a definite temperature, usually 15° C.

Densities of liquids are usually stated at a temperature of 15° C., but sometimes the densities are taken at higher temperatures, or may be compared with water, at 4° C. For example, alcohol at 20° C. has a density of 0·790, whereas at 15° C. the density is 0·794, when compared with water at 15° C. The relative temperatures should be stated in the following manner. Alcohol $\Delta = 0{\cdot}794$ (15°/15°), $\Delta = 0{\cdot}790$ (20°/15°). The densities given in this book are 15°/15°, unless otherwise stated.

The Determination of the Density of a Liquid may be carried out as follows :

An empty bottle, or other suitable vessel, is weighed in a perfectly clean and dry state. It is then filled to a fixed level with distilled water at 15° C., and is again weighed. The difference between the two weights gives the weight of the water which fills the bottle to the level.

The clean dry bottle is then filled in a similar way with the liquid at the temperature of 15° C. and is weighed again. By subtracting from this weight the weight of the bottle, the weight of the liquid is obtained.

Since the volumes of water and of the liquid which have been weighed are equal, the density of the liquid is obtained by dividing the weight of the liquid by the weight of the water. Thus, if

W = Weight of vessel + water,
W_1 = Weight of vessel + liquid,
W_2 = Weight of vessel alone.

$$\text{then the density of the liquid} = \frac{W_1 - W_2}{W - W_2}.$$

Two forms of apparatus which are used for ascertaining the density of a liquid by weighing it on the balance are the Specific Gravity Bottle (**18, 19**) and the Sprengel Tube (**20**); the use of the Hydrometer(**21**) dispenses with the necessity of weighing.



FIG. 17.—Density Bottle.

18. The Density or Specific Gravity Bottle (Fig. 17) consists of a small thin glass bottle, into the neck of which an accurately ground *blown-glass* stopper is fitted. The neck is contracted below the stopper and has a mark etched upon it. The mark enables the bottle to be always charged with precisely the same volume of liquid.

This form of bottle is useful for all liquids, but more especially for volatile liquids, since the stopper prevents the escape of vapour,

and consequent loss of weight, from occurring during the process of weighing.

Before the bottle is used it is thoroughly cleansed with distilled water, then dried in the steam oven, and is accurately weighed when it is cold. A more rapid method of drying the bottle consists in rinsing it out with alcohol, then with ether, and then placing it in the steam oven.

The bottle must now be filled to the mark with distilled water which has been brought to the temperature of 15° C. in a separate vessel. This is conveniently effected by filling the bottle with distilled water, the temperature of which has not been first adjusted, and then placing it in a bath of water which is kept at 15° C.

As soon as the distilled water in the bottle has assumed the standard temperature, which will take from twenty to thirty minutes, the excess of liquid is removed by a narrow pipette, until the meniscus just touches the mark. The dry stopper is then inserted, and the bottle is quickly but carefully dried with a clean dry cloth. The bottle and its contents are then weighed.

The difference between the weights of the bottle, when filled and when empty, gives the weight of the water at 15° C. which it contains when it is exactly filled up to the mark.

A precisely similar series of operations is now carried out with the liquid whose specific gravity is to be found. The weight of the liquid which fills the bottle to the mark is thus determined. By dividing this weight by the weight of the equal volume of water, already obtained, the density of the liquid is found.

19. Another Form of Specific Gravity Bottle which is suitable for non-volatile liquids is shown in Fig. 18. The neck of this bottle is fitted with a *perforated* stopper. The perforation enables the bottle to be precisely filled with the liquid, with the entire exclusion of air bubbles.

After the bottle has been filled with liquid, and the liquid has been brought to the requisite temperature, the stopper is dropped into the neck; the liquid will then *entirely fill* the bottle and the perforation in the stopper, a small quantity overflowing from the perforation. The bottle is then wiped dry and weighed.



FIG. 18.—Density Bottle.

A cloth may be used for wiping the surface of the bottle; but the top of the stopper should be wiped by the dry hand, since the porous cloth would absorb some of the liquid contained in

the capillary bore of the stopper, and lower the level of the liquid.

20. The Sprengel Tube is more generally used than the ordinary specific gravity bottle for taking the specific gravity of a liquid at a temperature differing from that of the atmosphere.

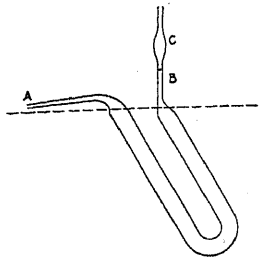


FIG. 19.—Sprengel Tube.

As is shown in Fig. 19, it consists of a broad vessel into which two thick-walled capillary tubes are fused. The two capillary tubes are bent at obtuse angles and a small bulb C is blown on one limb. A mark B is made just below the small bulb. The other limb A terminates in a fine opening. The liquid is introduced into the tube, and the latter is immersed in a beaker of water maintained at the desired temperature until the whole is at constant temperature. The tube is then inclined and a piece of filter paper placed in contact with the end of tube A until the liquid in the other limb just reaches the mark B. The tube is then placed in a vertical position. The liquid recedes from the limb A and rises in B. Should the temperature rise before or during weighing the small bulb offers sufficient space to contain the liquid without overflowing. The outside of the tube is then carefully dried and the whole weighed.

The tube is emptied and dried, and is exactly filled with water to the mark, as already described, and again weighed.

EXPERIMENT 11.—Determine the density of a sample of petroleum by the specific gravity bottle, and control the determination by means of the Sprengel tube.

21. The Hydrometer furnishes a rapid means of taking the density of a liquid substance, and dispenses altogether with the process of weighing. It is a glass or metal float (Fig. 20), which is weighted below so as to cause it to assume a vertical position when it is placed in the liquid whose specific gravity is to be determined. The stem is so graduated that the number which is level with the surface of the liquid, when the hydrometer

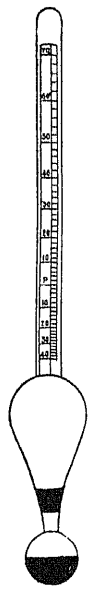


FIG. 20.—Hydrometer.

is floating freely, shows the specific gravity of the liquid. The temperature of the liquid must be adjusted to the temperature at which the hydrometer has been graduated, which is usually 15° C.

The accuracy of the graduation may be ascertained by floating the hydrometer in liquids, the densities of which have been determined by accurate weighing (**18–20**).

NOTE.—A Rapid Method for the determination of the approximate density of a liquid is described in paragraph **260.** This method, which involves the use of only a very little of the liquid, is specially applicable to the identification of that liquid.

DETERMINATION OF THE DENSITY OF A SOLID

22. The density of an organic solid is best determined by means of a specific gravity bottle (Figs. 17 and 18) and a liquid of known density in which the solid is relatively insoluble. Many organic solids are comparatively insoluble in water, or in "toilet paraffin," or in a solution of salt. Any liquid in which the solid is only sparingly soluble may be used, provided that it is first saturated with the substance under examination.

It is best, in those cases where the solid melts without decomposition, to first fuse the solid in a small porcelain dish and then pour it out on to a porcelain tile to solidify. The compact product thus obtained is then broken into pieces sufficiently small to be put into the specific gravity bottle.

First weigh the empty and dried bottle, and then weigh it again when the bottle is full of the liquid in which the solid is insoluble. The bottle should be filled at a known temperature. Half fill the dried bottle with the solid and again weigh, and then almost fill it up with the liquid. Attach the bottle to a vacuum pump and exhaust it so as to remove any bubbles of air that cling to the solid. Fill the specific bottle exactly, at the same temperature as before, and reweigh. Thus, if

W_1 = Weight of the empty bottle,
W_2 = Weight of bottle full of the liquid,
W_3 = Weight of bottle and the solid,
W_4 = Weight of the bottle, solid and liquid,
D = Density of liquid,

then the weight of solid in air $= W_3 - W_1$, and the apparent weight of the liquid which occupies the same volume as the solid

$$= W_2 + W_3 - W_1 - W_4$$

and hence the density, $= \dfrac{W_3 - W_1}{W_2 + W_3 - W_1 - W_4} \cdot D.$

EXPERIMENT 12.—Determine the density of naphthalene or of anthraquinone by weighing in distilled water.

REFRACTIVE INDEX

23. The determination of the refractive index is of great importance in examining the purity of organic liquids and in the detection of adulterants. The refractive index is of particular importance in the analysis of oils, and its measurement requires only a small quantity of the fluid. The determination is made usually either with the **Abbé** refractometer or the **Pulfrich** refractometer.

DETERMINATION OF REFRACTIVE INDEX BY THE ABBÉ REFRACTOMETER

24. In this instrument the prisms of the refractometer are kept at a constant temperature, say, 20° or 25° C., by means of water circulated from a thermostat. The reflecting mirror is arranged so that the cross wires are illuminated, and then the telescope is sharply focused on them. The double prism is then opened by means of the screw adjustment and cleaned with soft cotton wool damped with ether. A few drops of the oil are placed on the horizontal surface of the fixed prism and the two prisms tightly closed together again. The instrument is then adjusted until the field of vision shows the boundary between light and shade at the intersection of the cross wires. This boundary line must be adjusted as sharply as possible, and then the index of refraction is read off directly on the scale. The temperature correction for oils and fats is approximately 0·0004 for each degree Centigrade.

After use the prisms should be carefully cleansed and protected from damage by scratching by placing a piece of filter paper between them. The instrument is in correct adjustment when water at 18° C. gives a value of 1·333.

EXPERIMENT 13.—Determine the refractive index of turpentine and of glycerol by the Abbé refractometer.

DETERMINATION OF REFRACTIVE INDEX BY THE PULFRICH REFRACTOMETER

25. In this form of refractometer the liquid under examination is placed in a cell cemented to the top of a right-angled glass prism, the refractive index of which must be known and must be greater than that of the liquid. Both the prism and the liquid are maintained at a uniform temperature by circulating water from a thermostat through a jacket encasing the prism and through a tube immersed in the liquid in the cell.

The prism, carrying its glass cell, is screwed into position with the plane face of the prism towards the observation telescope. A sodium flame is used normally as a source of light, since the value of the index of refraction varies with the wavelength of the light employed (see paragraph **26**). The light is so placed that it is reflected from the reflecting prism and throws an image of the flame on to the side of the cell placed on the top of the refracting prism. To exclude extraneous light, and to act as a thermal insulator, a wooden cap is placed over the cell, the light entering by means of a notch cut in the side. The cell should be filled with the liquid under examination to a depth of a quarter of an inch. When the temperature is constant the disc is rotated until the beam of refracted light is visible as a yellow band of light across the field of view. The disc is then clamped and the cross wires focused by rotating the eyepiece, and by means of the fine-adjustment screw the intersection of the wires is made to coincide with the upper edge of the light band. The mean of several determinations is taken. The refractive index is then read off from tables supplied with the instrument or calculated from the formula

$$r = \sqrt{N^2 - \sin^2 i}$$

where N is the index of refraction of the glass prism and i is the angle at which the light emerges from the prism.

The determination having been completed, the cell is emptied of liquid by means of filter paper, and the greatest care taken not to scratch the upper surface of the prism.

EXPERIMENT 14.—Determine the refractive index of acetone and of ethyl alcohol for sodium light (D line) by means of the Pulfrich refractometer.

OPTICAL ACTIVITY

26. Compounds containing an asymmetric carbon atom are optically active and have the power of rotating a beam of polarised light. Those compounds that rotate the beam of light to the right are termed dextro-rotatory and those that rotate to the left are termed lævo-rotatory.

The measurement of the degree of optical activity affords evidence of the purity of a compound and also a method of estimating the concentration of solutions of active substances of known rotatory power.

The instrument used for the determination of optical rotation

is called a polarimeter. The instrument (Fig. 21) consists essentially of two Nicol prisms A and B, one of which, A, can be rotated about the common axis. The first prism, B, by which the light is polarised is called the polariser, and the second, A, by which it is examined, is termed the analyser.

A thin quartz plate D is interposed so as to obscure part of the field. The tube C, the observation tube, contains the solution under examination. The sodium flame is used as a source of monochromatic light, and is conveniently produced by allowing the hot flame of a Bunsen burner to pass through a small hole in a piece of asbestos card, on which is heaped sodium bromide.

The angle through which the analysing prism is rotated can be read by means of a graduated circular scale, provided with a vernier

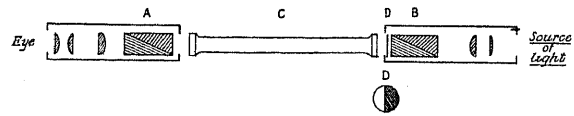


FIG. 21.—Section of Polarimeter.

and a small movable microscope. The instrument is in adjustment when each half of the visible disc is equally illuminated. Observations are made with C, at first full of distilled water and then full of the liquid under examination. The difference between the two readings gives the observed angle of rotation.

The degree of rotation depends on (i.) the substance used, (ii.) the length of the observation tube, (iii.) the wavelength of the light employed, and (iv.) the temperature. The *specific rotation* $[a]$ of a liquid is given by the equation

$$[a] = \frac{a}{l \cdot d}$$

Where l is the length of the column of liquid in decimetres, d is the density, and a is the observed angle of rotation. It is usual to indicate the nature of the light employed and the temperature in the following manner :

$$[a]_D^{20} = \frac{a}{l \cdot d}$$

Thus $[a]_D^{20}$ represents the specific rotation at 20° C. and for the *D* line (sodium light).

When a solution is employed the concentration must be taken into account, hence

$$[a] = \frac{100 \cdot a}{l \cdot c}$$

$$\text{or} = \frac{100 \cdot a}{l \cdot p \cdot d}$$

Where c is the number of grams of the active substance in 100 c.c. of solution and p is the number of grams of the active substance in 100 gm. of the solution of density d.

The number of grams x of the substance in a 100 c.c. of the solution may be calculated from the formula

$$x = \frac{100 \cdot a \cdot}{l\,[a] \cdot}$$

In the case of some of the sugars, such as dextrose, the rotation

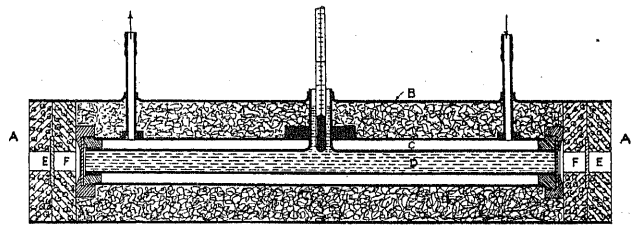


FIG. 22.—Observation Tube of Polarimeter, Maintained at Constant Temperature.

of a freshly prepared solution rapidly diminishes on standing, owing to isomeric changes in structure. Such a change is termed Mutarotation, and is instantly effected in the case of dextrose by the addition of a trace of alkali.

In using the polarimeter care must be taken to keep the observation tube at a constant temperature, as otherwise convection currents are set up in the liquid which completely obscure the transmitted light. It is advantageous to have the observation tube jacketed with water as shown in Fig. 22.

The observation tube D is surrounded by the constant temperature water jacket C, and insulated thermally by a cotton-wool wrapping B and cork end-pieces A,A, each containing a false end-piece of glass E,E, which enclose small pockets of air F,F, which serve to prevent radiation losses from the glass ends of the observation tube proper. Such an arrangement is essential when working at temperatures above 20° C. and in experiments in which the rate of change of rotation is measured. The water

in the jacket is fed in from a thermostat kept at the desired temperature.

EXPERIMENT 15.—Determine the specific rotation of cane sugar, using a 10 per cent. solution.

EXPERIMENT 16.—Determine the specific rotation of a freshly prepared solution of dextrose, and also of the same solution after the addition of a little caustic soda solution.

SECTION II

THE PREPARATION OF ORGANIC COMPOUNDS

30. Introductory Remarks.—The preparations described have been selected with the object of making the experimenter familiar with the more usual processes employed in organic preparations and with the standard methods of organic synthesis. To this end the preparations have been arranged in families of related compounds, and not in the disconnected order which would result if they were arranged in order of increasing difficulty.

The groups are :—

Hydrocarbons, Halogen Compounds, Alcohols, Phenols, Aldehydes, Ketones, Acids, Acid Anhydrides, Ethers, Esters.

Amides and Substituted Amides, Nitriles, Nitroso-Compounds, Nitro-Compounds, Amines.

Sulphonic Acids, Azoxy-, Azo-, Hydrazo- and Hydrazine Compounds, Oximes, Dyes, Carbohydrates and Osazones.

As far as possible the reactions given are of a perfectly general nature, and may be applied to the preparation of related compounds.

The chemical principles underlying each synthesis are given fully, and as they should be understood by the student *before* carrying out the preparation, they are given in the paragraph preceding the description of the practical work. The general methods of preparing each family of compounds are given at the commencement of each sub-section.

It is most important that the student should record the yield obtained and the essential physical characteristics of each substance prepared.

HYDROCARBONS

31. The more important methods of synthesis of the hydrocarbons are those associated with the names of Fittig, and with Friedel and Craft. Hydrocarbons are also produced by the reduction of such compounds as alcohols and ketones, and in the aromatic series, by the elimination of amino-groups by diazotisation and subsequent reduction with stannous chloride.

PREPARATION 1. ETHYL BENZENE, $C_2H_5 . C_6H_5$.

32. Reaction (Fittig's Synthesis).—The Wurtz synthesis of aliphatic hydrocarbons, by the action of sodium on the alkyl halides, was applied by Fittig to the preparation of aromatic hydrocarbons.

$$C_6H_5Br + C_2H_5Br + 2Na \rightarrow 2NaBr + C_2H_5 . C_6H_5$$

Two aromatic halides may also be made to unite in the same way.

33. Preparation.—Place 100 c.c. of ether in a separating funnel, and wash twice successively with half its volume of water. Transfer the ether to a stoppered cylinder and dry it by the addition of pieces of anhydrous calcium chloride. After some hours filter the alcohol-free dry ether from the calcium chloride.

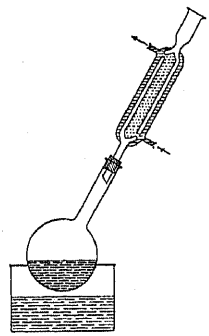


FIG. 23.—Reflux Apparatus.

Place the dry ether in a 500-c.c. round-bottomed flask, and add 18 gm. of metallic sodium in the form of wire, or very thin slices. Immerse the flask in some cold water, and fix to it a reflux condenser, as shown in Fig. 23.

When no more hydrogen is evolved pour into the flask a mixture of 40 gm. of dry brombenzene and 34 gm. of dry ethyl bromide. Leave over night, or until the reaction is completed.

Decant the ethereal solution from the sodium bromide in the flask and rinse the flask successively with two small quantities of dry ether. Distil the ethereal solution on a water bath to remove the ether, and fractionally distil the residue through an air condenser, collecting the portion boiling between 133–136° C. Yield, 16 gm.

Caution.—When sodium is brought into contact with a limited amount of water it is liable to explode. To avoid this danger the residue of sodium and sodium bromide in the flask is removed carefully, and added cautiously in small quantities to cold water contained in a large pneumatic trough.

Ethyl benzene is a colourless liquid, insoluble in water, B.P. 136° C.; $\Delta = 0{\cdot}883$. For tests, see paragraph **298.**

PREPARATION 2. **TRIPHENYLMETHANE,** $(C_6H_5)_3CH$.

34. Reaction.—Friedel and Craft showed that alkyl groups can be attached to aromatic hydrocarbons by the action of anhydrous aluminium chloride on alkyl halides and a hydrocarbon. The exact function of the aluminium chloride is not known, but the reaction is to a certain extent reversible.

$$C_6H_6 + C_2H_5Br \rightarrow C_6H_5C_2H_5 + HBr$$
$$3C_6H_6 + CHCl_3 \rightarrow (C_6H_5)_3CH + 3HCl$$

If, instead of alkyl halides, acid chlorides are used, then ketones are produced.

$$C_6H_6 + CH_3COCl \rightarrow \underset{\text{Acetophenone}}{CH_3COC_6H_5} + HCl$$

See paragraph **94.**

35. Preparation.—Dehydrate a mixture of 120 gm. of benzene and 25 gm. of chloroform by allowing it to stand over solid calcium chloride for twelve hours. Filter the liquid into a round-bottomed flask fitted with a reflux condenser (Fig. 23, page 24) and place the apparatus in a draught chamber. Add gradually 20 gm. of anhydrous aluminium chloride (3 gm. every five minutes). The reaction commences spontaneously and hydrogen chloride is evolved.

Boil gently on a water bath for half an hour to complete the reaction. Pour the product, when cold, into cold water and separate the upper layer, which consists of triphenylmethane dissolved in an excess of benzene. Distil off the excess of benzene over the water bath. Heat the residue to about 150° C. to drive off moisture, and then distil it under reduced pressure (paragraph **10**). At first crude diphenylmethane distils over as an oil, and then the triphenylmethane as a bright coloured oil that solidifies in the receiver. Recrystallise the solid product twice from methylated spirit, decolorising with animal charcoal (**2–4**). Triphenylmethane will crystallise in the form of leaflets. Yield, 15 gm.

Triphenylmethane is a colourless solid, M.P. 92°; B.P. 358°. For tests, see paragraph **297.**

PREPARATION 3. **DIPHENYLMETHANE,** $(C_6H_5)_2CH_2$.

36. Reaction.—Hydrocarbons may be prepared by the complete reduction of such compounds as acids, ketones, aldehydes and alcohols. In the preparation of diphenylmethane, benzophenone is reduced with hydriodic acid. The yield is almost quantitative.

$$2HI \rightarrow H_2 + I_2$$
$$C_6H_5 . CO . C_6H_5 + 4H \rightarrow C_6H_5 . CH_2 . C_6H_5 + H_2O$$

Hydriodic acid is a most powerful reducing agent, and may be used for the reduction of all the classes of compounds given above. Its effect is increased by the addition of phosphorus, which by its reaction with the liberated iodine yields a further supply of hydriodic acid.

$$2P + 3I_2 \rightarrow 2PI_3$$
$$PI_3 + 3H_2O \rightarrow H_3PO_3 + 3HI$$

37. Preparation.—Seal a mixture of 12 gm. of benzophenone, 3 gm. of red phosphorus, and 12 gm. of concentrated hydriodic acid (" constant boiling " acid, B.P. 127° C.) in a bomb tube, in the manner described for the estimation of halogen by the Carius method (paragraph **406**). Heat the tube in the bomb furnace for five hours at a temperature of 170° C. When cold remove the tube from the furnace and open as described in paragraph **406**. Transfer the contents to a separating funnel and shake up with ether. Wash the ethereal solution three times with water, filter, and distil off the ether on a water bath (Fig. 5, page 4). Distil the residue under reduced pressure (at 80 mm., B.P. = 175°). On cooling the distillate the diphenylmethane solidifies. Yield, 9 gm.

Diphenylmethane is a colourless solid with an agreeable orange-like odour. M.P. 26°; B.P. 261° C.; $\Delta = 1{\cdot}001$ (26°/4°). For tests, see paragraph **297**.

PREPARATION 4. **BENZENE,** C_6H_6.

38. Reaction.—Primary aromatic amines when treated in *ice-cold* solution with nitrous acid yield diazo-compounds. This reaction was discovered by Peter Griess in 1860. The diazonium salts are very unstable and explosive when dry, but undergo a number of important transformations in aqueous solution.

$$C_6H_5NH_2 + HNO_2 + HCl \rightarrow \underset{\text{Diazobenzene chloride}}{C_6H_5N : NCl} + 2H_2O$$

The diazonium group may be replaced by—

(i.) *Hydroxyl* by warming the aqueous solution. See paragraphs **76, 77.**

$$C_6H_5N : NCl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

(ii.) *Halogens and Cyanogen* by warming with appropriate cuprous salt (Sandmeyer's Reaction). See paragraphs **53, 54.**

$$C_6H_5N : NCl + CuCl \rightarrow C_6H_5Cl + N_2 + CuCl$$
$$C_6H_5N : NCl + CuCN \rightarrow C_6H_5CN + N_2 + CuCl$$

(iii.) *Hydrogen*, by reduction with alcohol, alkaline stannous chloride, or hypophosphorous acid.

$$C_6H_5N : NCl + SnCl_2 + 5KOH \rightarrow C_6H_6 + N_2 + 3KCl + K_2SnO_3 + 2H_2O$$
$$C_6H_5N : NOH + C_2H_5OH \rightarrow C_6H_6 + N_2 + CH_3CHO + H_2O$$

(iv.) *Acyl groups* by the action of aluminium chloride on a warm solution of the diazonium compound in an aromatic hydrocarbon

$$C_6H_5N : NCl + C_6H_6 \rightarrow C_6H_5 . C_6H_5 + N_2 + HCl$$

For other reactions of the diazonium compounds, see preparation of para-chlortoluene (**53, 54**); phenol (**76, 77**); methyl orange (**218, 219**); Orange II (**220, 221**); and phenylhydrazine (**223, 224**).

39. Preparation.—In this preparation the process of diazotisation is first performed, which is followed by reduction.

Diazotisation.—Dissolve 10 gm. of aniline in a mixture of 25 c.c. of concentrated hydrochloric acid and 50 c.c. of water, and cool with ice. Add cautiously an ice-cold solution of 10 gm. of sodium nitrite in 30 c.c. of water, until a spot of the solution just gives a blue colour with starch-potassium-iodide paper. This indicates the presence of free nitrous acid, of which a large excess must be avoided.

Reduction.—Slowly add the above solution of diazo-benzene chloride to an ice-cold solution of 20 gm. of caustic soda in 60 c.c. of water. To a solution of 40 gm. of stannous chloride in 100 c.c. of water, add concentrated caustic soda solution until the precipitated stannous hydroxide is redissolved. Treat the alkaline diazo-solution with successive small quantities of the stannite solution, keeping the whole ice-cold and allowing the action to moderate before making a further addition. When the whole of the stannite solution has been added distil the mixture from a flask until no more benzene is condensed. Separate from the heavier aqueous layer and redistil at 75–85° C. Yield, 10 c.c.

Benzene is a colourless liquid, insoluble in water. B.P. = 80·4° C.; $\Delta = 0{\cdot}874$ (20°/4°). For tests, see paragraph **298.**

HALOGEN COMPOUNDS

40. The more important methods of preparation of halogen compounds include—

(i.) *The replacement of hydrogen* by means of halogen, or by the use of a halogen compound such as the halides of phosphorus or sulphur (see paragraphs **41–46**).

(ii.) *The addition of halogen or halogen acid to an unsaturated compound, e.g.,*

$$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$$

(iii.) *The replacement of the — OH group* by means of the halogen acid and a dehydrating agent, or by the use of the phosphorus halides (see paragraphs **47–52**).

(iv.) *The replacement of the diazo-group by halogen,* by the methods of Griess, Sandmeyer or Gatterman (see paragraphs **53–56**).

Preparation 5. **CHLORACETIC ACID,** $CH_2Cl \cdot COOH$.

41. Reaction.—The direct replacement of hydrogen atoms by a halogen is usually too slow to be of practical importance unless a *halogen carrier* is present. For this purpose iron, the halides of iron, aluminium, phosphorus, sulphur, antimony and iodine are frequently employed.

In halogenating fatty acids the halogen always replaces the hydrogen attached to the α-carbon atom.

$$CH_3 \cdot CH_2 \cdot COOH + Cl_2 \rightarrow CH_3 \cdot CHCl \cdot COOH + HCl$$

and until all the α-hydrogen atoms have been replaced the halogen does not react elsewhere in the compound.

Halogenation greatly increases the relative strength of the acid.

42. Preparation.—Place 50 c.c. of glacial acetic and 5 gm. of sulphur in a tubulured retort and weigh the whole. Support the retort on a sand bath with the neck tilted upwards at an angle of about 30° and attached to a reflux condenser, closed at the upper end with a calcium chloride drying tube. Carry out the experiment in the fume cupboard, and, if possible, in sunlight or bright daylight.

Keep the acid gently boiling and lead a stream of dry chlorine

into the retort by a tube reaching nearly to the bottom of the liquid. Continue until an increase of weight of 20 gm. has taken place.

Pour off the liquid from the sulphur and distil, collecting the fraction boiling between 170–190° C., which contains the chloracetic acid. Pour off any liquid from the solid distillate and redistil, collecting the fraction between 180–190° C. Yield, 45 gm.

Monochloracetic Acid is a colourless, sharp smelling, crystalline solid that blisters the skin. M.P. 62°; B.P. 189°. For tests, see paragraph **302**.

PREPARATION 6. **CHLORBENZENE**, $C_6H_5 . Cl$.

43. Reaction.—The direct halogenation of aromatic compounds in the cold effects substitution in the nucleus, but at higher temperatures the halogenation occurs in the side chain.

$$C_6H_5CH_3 \xrightarrow{\text{Cold}} C_6H_4Cl . CH_3 \quad \text{Chlortoluene.}$$

$$C_6H_5CH_3 \xrightarrow{\text{Hot}} C_6H_5 . CH_2Cl \quad \text{Benzyl chloride.}$$

A halogen carrier is always used (see paragraph **41**).

Obviously the chlorination of benzene can only result primarily in the formation of chlorbenzene.

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

but when about half the benzene has been chlorinated considerable quantities of the isomeric *o*- and *p*-dichlorbenzenes are produced. The reaction is therefore stopped at this stage.

44. Preparation.—Place 100 c.c. of benzene and 2 gm. of reduced iron in a round-bottomed flask, fitted with a reflux condenser (Fig. 23, page 24). Pass in dry chlorine until the increase in weight is 35 gm., maintaining the temperature at about 40–45° C. by first cooling and then, if necessary, by gently warming. Fractionate the liquid, using a column (Fig. 8, page 6). Unchanged benzene first distils, then monochlorbenzene between 130–135° (air condenser), and, finally, the dichlorbenzenes, from which, on cooling, the greater part of the para-isomer will crystallise.

Monochlorbenzene is a colourless liquid; B.P. 132°; Δ = 1·113 (15°). For tests, see paragraph **303**.

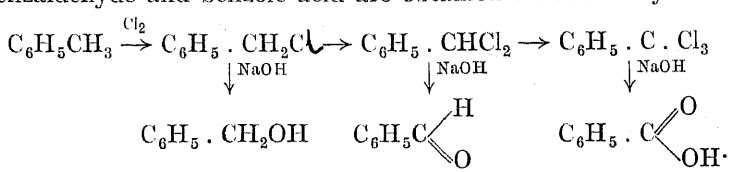
o-Dichlorbenzene, colourless liquid; M.P. 14°; B.P. 179°; Δ = 1·327 (0°). For tests, see paragraph **303**.

p-Dichlorbenzene, colourless solid; M.P. 53°; B.P. 174°. For tests, see paragraph **302**.

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PREPARATION 7. **BENZYL CHLORIDE,** $C_6H_5 . CH_2Cl$.

45. Reaction.—As stated in paragraph **43**, the halogenation of aromatic side-chain compounds at high temperatures effects substitution in the side chain. By the chlorination of boiling toluene, benzyl chloride, benzal chloride and benzotrichloride are produced, and by the hydrolysis of these compounds benzyl alcohol, benzaldehyde and benzoic acid are obtained commercially—



The usual halogen carrier employed is phosphorus pentachloride.

46. Preparation.—Place 50 c.c. of toluene and 3 gm. of phosphorus pentachloride in a tubulured retort, attached to a reflux condenser, as described in paragraph **42.** Close the end of the condenser with a calcium chloride drying tube and pass in dry chlorine until there is an increase of weight of 16 gm.

Pour off the liquid and fractionate, collecting the distillate boiling between 165–185° C. Carefully refractionate, using a column to obtain the fraction boiling at 176–180° C. Yield, 40 gm.

Benzyl chloride is a colourless liquid, with an irritating smell and painful effect upon the eyes. B.P. = 179° ; $\Delta = 1{\cdot}104$ (15°). For tests, see paragraph **303.**

PREPARATION 8. **ETHYL BROMIDE,** C_2H_5Br.

47. Reaction.—The oxygen of ketones, aldehydes and acid amides, and also the hydroxyl in alcohols, phenols, carboxylic and sulphonic acids, can usually be replaced by halogen atoms by the use of such reagents as the halides of phosphorus. This replacement may, in some cases, be effected by treatment with the appropriate halogen acid and a dehydrating agent, such as concentrated sulphuric acid or anhydrous zinc chloride.

Alkyl hydroxyl groups are best, (*a*) *chlorinated* by the action of anhydrous hydrochloric acid and zinc chloride ; (*b*) *brominated* by the action of strong sulphuric acid and potassium bromide ; and (*c*) *iodinated* by the agency of phosphorus and iodine.

$$H_2SO_4 + KBr \rightarrow KHSO_4 + HBr$$

$$C_2H_5OH + HBr \xrightarrow{H_2SO_4} C_2H_5Br + H_2O$$

48. Preparation.—Add cautiously, small portions at a time,

25 c.c. of alcohol to 40 c.c. of concentrated sulphuric acid, shaking and cooling between each addition. Pour the well-cooled mixture on to 60 gm. of finely powdered potassium bromide contained in a round-bottomed flask fitted with a reflux condenser (Fig. 23, page 24) and leave overnight. Distil the mixture from a water bath, using a water condenser. Transfer the distillate to a separating funnel and wash the ethyl bromide with a dilute solution of sodium carbonate and then thoroughly with water. Dehydrate the separated ethyl bromide with anhydrous calcium chloride and redistil at 37–39°. Yield, 55 gm.

Ethyl Bromide is a heavy, colourless liquid, insoluble in water. B.P. 38° C.; $\Delta = 1{\cdot}450$ (15°). For characteristic tests, see paragraph **305**.

Preparation 9. **ETHYL IODIDE,** C_2H_5I.

49. Reaction.—As shown in paragraph **47**, the replacement of alkyl hydroxyl groups by iodine is best carried out by the agency of phosphorus and iodine.

$$2P + 3I_2 \rightarrow 2PI_3$$
$$PI_3 + 3C_2H_5OH \rightarrow 3C_2H_5I + H_3PO_3$$

50. Preparation.—In a round-bottomed flask of 200 c.c. capacity place 50 c.c. of alcohol and 5 gm. of red phosphorus. Add 50 gm. of powdered iodine in small portions, cooling the flask by immersion in ice water. Attach a reflux condenser and leave at room temperature for eight hours. Then reflux on a water-bath for two hours to complete the reaction and finally distil off the ethyl iodide through a water condenser, immersing the distilling flask in rapidly boiling water. Wash the distillate first with dilute caustic soda solution and then several times with water. Dry with anhydrous calcium chloride and redistil, collecting between 70–74°. The addition of a few milligrams of dry, freshly precipitated, reduced silver will prevent subsequent discoloration due to the liberation of iodine. It should be kept in a well-stoppered bottle of brown glass. Yield, 60 gm.

Ethyl Iodide is a colourless, heavy insoluble liquid with a sweetish smell. It liberates iodine on keeping. B.P. = 72° C.; $\Delta = 1{\cdot}943$ (15°). For tests, see paragraph **307**.

Preparation 10. **ACETYL CHLORIDE,** $CH_3 . CO . Cl$.

51. Reaction.—The replacement of the hydroxyl group in carboxylic and sulphonic acids by chlorine, with the formation of the acid chlorides, is invariably accomplished by the use of the

phosphorus or sulphur halides (sulphuryl chloride being used commercially).

In general it is more advantageous to use phosphorus trichloride than the pentachloride, as the following equations will show :—

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$
$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + HCl + POCl_3$$

The pentachloride is used only in those cases where the trichloride does not react readily, or when the B.P. of the acid chloride obtained is near to that of the trichloride (76° C.), which would render the separation of the acyl chloride and the excess of the reagent difficult.

Phosphorus oxychloride can only be used with the dry salts.

$$2CH_3COONa + POCl_3 \rightarrow 2CH_3COCl + NaPO_3 + NaCl$$

52. Preparation.—To 60 gm. of glacial acetic acid contained in a dry 200 c.c. distilling flask, add, by means of a stoppered dropping funnel, 50 gm. of phosphorus trichloride. The flask must be well shaken after each addition, and kept cool by immersion in cold water. Warm the mixture to a temperature of 45° C. and keep it at that temperature until hydrogen chloride is no longer freely evolved.

Attach the flask to a dry condenser, leading by means of an adapter into a dry receiver (such as a suction flask) closed by a calcium chloride tube. Distil off the acetyl chloride by immersing the flask in rapidly boiling water. Replace the dropping funnel in this apparatus by a thermometer, and redistil the product, collecting between 50–55° C. Carefully protect from atmospheric moisture. Yield, 50 gm.

Acetyl Chloride is a pungent, strongly fuming liquid. B.P. 52° C. ; $\Delta = 1{\cdot}105$ (20°). For tests, see paragraph **303**.

PREPARATION 11. *p*-CHLORTOLUENE,



53. Reaction.—The diazo-group can be replaced by halogen by one of the following methods :—

(i.) *Griess.*—The solution of the diazonium salt is heated with the appropriate halogen acid. This method is only really satisfactory in the preparation of the iodides (see paragraph **55**).

(ii.) *Sandmeyer.*—The solution of the diazonium salt is run

slowly into a boiling solution of the cuprous salt in the appropriate halogen acid. [In the preparation of bromo- and iodo-derivatives diazotise in the presence of dilute sulphuric acid solution.]

$$C_6H_5N = NCl \xrightarrow[HCl]{Cu_2Cl_2} C_6H_5 . Cl + N_2$$

(iii.) *Gatterman.*—The solution of the diazonium salt of the corresponding acid is treated with finely divided copper powder or paste at the ordinary temperature.

54. Preparation.—Diazotise an ice-cold solution of 36 gm. of paratoluidine in 200 c.c. of water and 60 c.c. of hydrochloric acid with 23 gm. of sodium nitrite dissolved in 60 c.c. of water in the manner described in paragraph **39.**

Slowly run this solution into an almost boiling solution of 35 gm. of cuprous chloride in 250 c.c. of concentrated hydrochloric acid, to which has been added 100 c.c. of water. Keep the solution hot for half an hour, pour off the bulk of the aqueous liquid, and steam-distil the residual oil (Fig. 9, page 6). Wash the distilled oil in a separating funnel with a dilute solution of caustic soda and then once with water. Dehydrate with anhydrous calcium chloride and redistil through an air condenser (Fig. 6, page 5), collecting between 160–164° C. Yield, 32 gm.

para-**Chlortoluene** is a colourless liquid. B.P. = 162°; Δ = 1·070 (20°). For tests, see paragraph **303.**

Preparation 12. **IODOBENZENE,** C_6H_5I.

55. Reaction.—In this preparation the diazo-group is replaced by iodine by the method of *Griess* (see paragraph **53**, preparation 11). The aqueous solution of the diazonium salt is boiled with hydriodic acid.

$$C_6H_5N = NCl + HI \rightarrow C_6H_5I + HCl + N_2$$

56. Preparation.—Add 23 gm. of aniline to 300 c.c. of water and 40 c.c. of concentrated hydrochloric acid and diazotise by the method described in preparation 4, paragraph **39**, using a solution of about 20 gm. of sodium nitrite in fairly concentrated solution. Run in slowly with continual stirring a cold, concentrated solution of 40 gm. of potassium iodide. Nitrogen is readily evolved. Towards the end of the reaction warm very gently by immersing in tepid water. When no more gas is evolved remove any separated iodine by the addition of caustic soda

solution. Separate off the heavy oil and wash with water. Dehydrate with calcium chloride and distil through an air condenser. B.P. 188° C. Yield, 46 gm.

Iodobenzene is a heavy colourless oil. B.P. = 188° C.; Δ = 1·840 (15°). For tests, see paragraph **307**.

ALCOHOLS

57. The alcohols may be produced by the following general methods, which should be compared with the methods available for the preparation of the phenols (see paragraph **69**).

(i.) *The hydrolysis of esters*, by refluxing with aqueous solutions of alkalies. This method is only of importance in the preparation of the higher alcohols from natural fats and waxes, *e.g.*, glycerol, cetyl alcohol.

(ii.) *From the halogen compounds*, by boiling with dilute alkalies, or alkali carbonates (see preparation of benzyl alcohol (**58, 59**)).

(iii.) *The reduction of aldehydes and ketones* with such agents as sodium amalgam and water; sodium and alcohol; aluminium amalgam, or electrolytically (see preparation of isopropyl alcohol, paragraphs **60, 61**).

(iv.) *The condensation of aldehydes*, either by the aldol condensation or the benzoin condensation processes, see preparation of benzoin, paragraphs **62, 63.**

(v.) *From amines by the action of nitrous acid*, a reaction of more importance in the preparation of phenols, see paragraphs **76, 77.**

(vi.) *From unsaturated compounds by oxidation* with dilute potassium permanganate solution, or with hypochlorous acid, which results in the formation of a chlorhydrin.

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + HOCl \rightarrow \begin{matrix} CH_2Cl \\ | \\ CH_2OH \end{matrix}$$

(vii.) *The Grignard synthesis*, by the action of the Grignard reagent on aldehydes and ketones, etc. (see preparation of phenyl methyl carbinol, paragraphs **64–66**).

In addition, many alcohols, *e.g.*, ethyl alcohol, amyl alcohol, are obtained commercially by fermentation processes.

Preparation 13. **BENZYL ALCOHOL,** $C_6H_5 . CH_2OH$.

58. Reaction.—The halogen atoms in aliphatic compounds are much less firmly attached than is usually the case in the aromatic series, and can be replaced by boiling with aqueous solutions of alkali hydroxides or carbonates.

$$C_6H_5 . CH_2Cl + NaOH \rightarrow C_6H_5 . CH_2OH + NaCl$$

If more than one halogen atom is attached to the same carbon atom the hydrolysis is even more easily accomplished, but, of course, aldehydes, ketones or acids are obtained and not alcohols. Thus

$$C_6H_5 . CHCl_2 + 2NaOH \rightarrow C_6H_5CHO + H_2O + 2NaCl$$
$$C_6H_5 . CCl_3 + 3NaOH \rightarrow C_6H_5COOH + H_2O + 3NaCl$$
$$CH_3 . CCl_2 . CH_3 + 2NaOH \rightarrow CH_3COCH_3 + H_2O + 2NaCl$$

59. Preparation.—In a round-bottomed flask of 500 c.c. capacity, fitted with a reflux condenser, place 25 gm. of benzyl chloride (paragraphs **45, 46**) and a solution of 25 gm. of potassium carbonate in 200 c.c. of water. Reflux until the mixture no longer smells of benzyl chloride (about eight hours). Extract with ether and dehydrate the ethereal solution with anhydrous potassium carbonate. Pour off the ethereal solution, evaporate off the ether on a water bath, and then distil the benzyl alcohol through an air condenser, collecting between 204–207° C.

Benzyl Alcohol is a colourless liquid, with a faintly aromatic odour. Moderately soluble in water (4 per cent. at 17° C.). B.P. = 205° C.; $\Delta = 1{\cdot}043$ (20°). Reacts as an aliphatic alcohol. For tests, see paragraph **295**.

PREPARATION 14. **ISOPROPYL ALCOHOL,** $CH_3 . CHOH . CH_3$. **PINACONE HYDRATE,** $(CH_3)_2COH . COH . (CH_3)_2 + 6H_2O$.

60. Reaction.—Alcohols may be prepared by the reduction of aldehydes and ketones with mild reducing agents, such as sodium in ethyl or amyl alcohol, sodium amalgam in water and zinc dust in caustic soda solution or in acetic acid.

$$\underset{\text{Aldehyde}}{CH_3CHO} + 2\dot{H} \rightarrow \underset{\text{Primary alcohol}}{CH_3CH_2OH}$$

$$\underset{\text{Ketone}}{CH_3COCH_3} + 2\dot{H} \rightarrow \underset{\text{Secondary alcohol}}{CH_3 . CHOH . CH_3}$$

In the reduction of ketones, particularly in the aliphatic series and in acid solution, considerable quantities of pinacones are formed by condensation.

$$2(CH_3)_2CO + 2\dot{H} \rightarrow (CH_3)_2 . COH . COH . (CH_3)_2$$

61. Preparation.—Place 30 c.c. of acetone and 150 c.c. of water in a suction flask (since mercury is too heavy for a thin-walled vessel). Add, during the course of an hour, an amalgam of 30 gm. of sodium and 600 gm. (44 c.c.) of dry mercury. Cork the flask, leaving the side tube open. After twelve hours warm on the

water bath to 50° C. for half an hour, and then allow to cool. A pale coloured oil will be seen to have separated above the aqueous layer. Having separated off the mercury, extract twice with 30 c.c. of ether. Dry the ethereal extract with fused potassium carbonate. Distil off the ether gently on the water bath, and then the isopropyl alcohol, between 80–90° C. Disconnect from the condenser and distil the pinacone remaining in the flask directly into a cooled test tube, collecting between 170–180° C. Redistil the isopropyl alcohol, collecting between 81–83° C. Yield, 10 gm. Add to the pinacone an equal volume of hot water, heat up to boiling and allow to cool. The crystalline hydrate readily separates in white, four-sided, tabular crystals that sublime at the ordinary temperature. Yield, 8 gm.

Isopropyl Alcohol is a colourless liquid with a vinous odour, miscible with water. B.P. 82·8° C.; $\Delta = 0{\cdot}789$ (20°/4°). For tests, see paragraph **295.**

Pinacone is a colourless solid with a faint, peculiar odour, soluble in water. M.P. 35°. B.P. 172–173°.

Pinacone Hydrate is a white crystalline solid, soluble in hot water. M.P. 56° C. For tests, see paragraph **294.**

Preparation 15. **BENZOIN,** $C_6H_5CO \cdot CHOH \cdot C_6H_5$.

62. Reaction.—Two molecules of aromatic aldehydes may be made to condense together with the formation of a ketonic alcohol by the agency of potassium cyanide. The benzoin condensation does not take place with aliphatic aldehydes.

$$2C_6H_5 \cdot CHO \xrightarrow{KCN} C_6H_5CO \cdot CHOH \cdot C_6H_5$$

63. Preparation.—Reflux together on a water bath, placed in the fume cupboard, 40 gm. of benzaldehyde, 75 c.c. of absolute alcohol, and 8 gm. of potassium cyanide dissolved in 15 c.c. of water. Continue to reflux for one hour, and then allow to cool. Filter off the crystallised benzoin at the pump. Wash with a little water and recrystallise from dilute alcohol.

Benzoin is a colourless solid, crystallising in prisms. Slightly soluble in hot water, more easily in alcohol and ether. M.P. = 133°. For tests, see paragraph **291.**

Preparation 16. **PHENYL METHYL CARBINOL,** $C_6H_5 \cdot CHOH \cdot CH_3$.

64. Reaction.—By the action of the Grignard reagent (**65**) on aldehydes, ketones, esters, acid chlorides and anhydrides, alcohols

are obtained. The Grignard reagent, which is a magnesium alkyl halide, is readily formed by the action of magnesium on a solution of the selected alkyl halide (usually the iodide) in *anhydrous* ether.

The formation of the alcohol may be expressed by the equations :

$$\underset{\text{Formaldehyde}}{H . CHO} + R . Mg . I \rightarrow H . CHR . OMg . I \xrightarrow{H_2O} \underset{\text{Primary alcohol}}{R . CH_2OH} + Mg . I . OH$$

$$\underset{\text{Acetaldehyde}}{CH_3 . CHO} + R . Mg . I \rightarrow CH_3 . CHR . OMg . I \xrightarrow{H_2O} \underset{\text{Secondary alcohol}}{CH_3 . CHOH . R} + Mg . I . OH$$

$$\underset{\text{Acetone}}{CH_3 . CO . CH_3} + R . Mg . I \rightarrow (CH_3)_2 . CR . OMg . I \xrightarrow{H_2O} \underset{\text{Tertiary alcohol}}{(CH_3)_2 . CR . OH} + Mg . I . OH$$

65. Preparation of the Grignard Reagent.—Dissolve 36 gm. of dry methyl iodide in 50 c.c. of pure dry ether (dried with sodium wire or shavings). Add 20 c.c. of this solution to 6 gm. of clear magnesium ribbon placed in a flask fitted with a dropping funnel and a reflux condenser. If a vigorous reaction does not commence add a trace of iodine. When the action has moderated, add 100 c.c. of pure anhydrous ether and then the remainder of the methyl iodide solution, drop by drop, by means of the dropping funnel. Warm on the water bath until the solution of the magnesium is complete, which usually occupies one hour. Cool the contents of the flask with ice.

66. Preparation of Phenyl Methyl Carbinol.—Surround the flask, fitted with a tap funnel, by ice-water and slowly add, with constant shaking, a solution of 26 gm. of benzaldehyde dissolved in 25 c.c. of pure ether. The white solid magnesium compound will separate. Allow to stand for eight hours, and then add sufficient Normal hydrochloric acid solution (about 500 c.c.) to the contents of the flask, which is surrounded with cold water, so as to just dissolve the precipitate. Separate the ethereal layer and wash it with sodium bicarbonate solution, then with sodium bisulphite solution to remove the iodine, and again with sodium bicarbonate solution. Dehydrate with solid potassium carbonate, and distil off the ether on a water bath. Finally distil the residue under greatly reduced pressure. Yield, 22 gm.

Phenyl Methyl Carbinol is a colourless liquid. B.P. 203° C. $\Delta = 1{\cdot}013$.

PREPARATION 17. **ALLYL ALCOHOL**, $CH_2 : CH . CH_2OH$.

67. Reaction.—By heating together glycerol and oxalic acid at a temperature of about 110° C., formic acid is the principal product, the oxalic acid decomposing into carbon dioxide and formic acid, with the intermediate formation of glycerol monoformic ester.

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} COOH \\ | \\ | \\ COOH \end{array} \rightarrow \begin{array}{l} CH_2OCH . O \\ | \\ CHOH \\ | \\ CH_2OH + CO_2 + H_2O \end{array} \xrightarrow{H_2O} \begin{array}{l} CH_2OH \\ | \\ CHOH + H . COOH \\ | \\ CH_2OH \end{array}$$

At a higher temperature the glycerol is decomposed, forming the unsaturated allyl alcohol as shown below.

$$\begin{array}{l} CH_2OCH . O \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow{200° C.} \begin{array}{l} CH_2 \\ \| \\ CH + CO_2 + H_2O \\ | \\ CH_2OH \end{array}$$

Formic acid may be substituted for oxalic acid in this preparation.

68. Preparation.—Place a mixture of 240 gm. of glycerol, 50 gm. of oxalic acid and 0·5 gm. of ammonium chloride in a tubulured retort. Through the tubulure of the retort place a thermometer, the bulb dipping into the liquid, but not touching the bottom of the retort. Heat on a sand bath, when carbon dioxide will be readily evolved. When the temperature reaches 200° C. change the receiver, which will contain some aqueous formic acid. Continue the heating until the temperature reaches 250°. An oily distillate, with a disagreeable odour, will collect in the receiver. Redistil the distillate from a small flask over a naked flame until about 75 per cent. has been collected. Saturate the product with solid potassium carbonate, and separate the oily layer of allyl alcohol. Redistil this liquid, collecting the distillate between 95°–97° C. Yield, 18 gm.

Allyl Alcohol is a colourless liquid, with a pungent mustard-like odour, miscible with water. B.P. 96·6° C.; $\Delta = 0{\cdot}871$ (0°). For tests, see paragraph **295**.

PHENOLS

69. The Phenols may be prepared by the following general methods, which should be compared with those available for the synthesis of the alcohols (see paragraph **57**).

(i.) *From the halogen compounds.*—Halogens present in the benzene nucleus are usually more firmly attached than in the aliphatic series. It is only possible to replace nuclear halogen atoms by alcoholic potash, or by the sodium alcoholates when there are also present electronegative groups ($-OH$, $-NO_2$) in the ortho- or para-positions. With groups in the meta-position this replacement is not effected. Thus, while the halogen in chlorbenzene and 1 : 3 chlornitrobenzene cannot be displaced except with the greatest difficulty, it is comparatively easy to substitute the halogen in the 1 : 2 and 1 : 4 chlornitrobenzenes (see paragraphs **70**, **469**).

When more than one other electronegative group is present the substitution is even more easy. Thus, chlordinitrobenzene is hydrolysed by caustic soda, and picryl chloride by hot water (see preparation of dinitrophenol (**70**, **71**)).

(ii.) *From the sulphonic acids.*—Phenols are produced readily by the fusion of sulphonic acids with caustic alkali (see preparation of β-naphthol (**72**, **73**), and of alizarine (**74**, **75**)).

(iii.) *From the amines, by diazotisation*, subsequently warming the diazonium salt with water (see preparation of phenol (**76**, **77**)).

(iv.) *From the amines directly* by hydrolysis with acid or caustic alkali, when a negative substituent such as a nitro-group is present in the ortho- or para-position to the amino-group. Thus, whereas phenol cannot be obtained by the action of caustic soda on aniline, yet the nitrophenols are readily obtained from the ortho- and para-nitranilines.

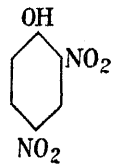
(v.) *By the reduction of aldehydes and ketones.*—The reduction may be effected by the use of reducing agents such as sodium in alcohol, sodium amalgam, zinc and caustic soda or acetic acid, sulphurous acid, sodium hydrosulphite, or hydrogen in the presence of a catalyst such as finely divided nickel (see preparation of quinol (**78**, **79**)).

(vi.) *From the aldehydes by condensation.*—When formaldehyde is condensed with a phenol, in the presence of a powerful condensing agent such as the caustic alkalies, dihydroxy-derivatives of

diphenylmethane are produced, the entering group taking preferably the para-position (alternatively the ortho-) to the hydroxy-group.

$$2C_6H_5OH + HCHO \rightarrow H_2O + HO \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4OH$$

PREPARATION 18. 2 : 4 **DINITROPHENOL,**



70. Reaction.—Aromatic halogen compounds containing negative groups in the ortho- or para-position to the halogen atom may be converted to the corresponding phenols readily, see paragraph **69** (i.). In fact, the relative amount of the meta-isomer in a mixture of ortho-, meta- and para-disubstituted halogen compounds may be found by estimating the relative amount of halogen that is not removed by alkali under suitable conditions (see paragraph **469**). Such compounds as dinitrophenol are obtained commercially in this way, as the dinitration of phenols results in the production of large quantities of tarry products.

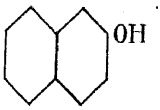
Sodium methoxide in alcohol is used to remove the chlorine atom in compounds such as *o*-chlornitrobenzene, but caustic alkalies or alkaline carbonates in aqueous solution are sufficient in the case of dinitro-derivatives.

$$Cl \cdot C_6H_4NO_2 + NaOCH_3 + H_2O \rightarrow NaCl + CH_3OH + HO \cdot C_6H_4 \cdot NO_2$$

$$Cl \cdot C_6H_3(NO_2)_2 + NaOH \rightarrow NaCl + HO \cdot C_6H_3 \cdot (NO_2)_2$$

71. Preparation.—Reflux together over a wire gauze 20 gm. of 2 : 4 dinitrochlorbenzene, 200 c.c. of water and 12 gm. of caustic soda until complete solution is obtained. Allow to cool and acidify with hydrochloric acid. Filter off the precipitated dinitrophenol by means of a Buchner funnel and pump, and recrystallise from dilute alcohol. First dry in the steam oven and then in a vacuum desiccator. Yield, 16 gm.

2 : 4 **Dinitrophenol** crystallises in very pale yellow needles. Volatilises in a current of steam. Soluble in hot water, in caustic alkalies, and in alcohol. M.P. 114° C. For tests, see paragraph **319**.

PREPARATION 19. **β-NAPHTHOL,** 

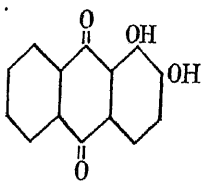
72. Reaction.—The aromatic sulphonic acids are directly converted to phenols by fusion with caustic alkalies, preferably caustic potash.

$$C_6H_5SO_3Na + NaOH \rightarrow C_6H_5ONa + NaHSO_3$$

In the benzene series the alkaline fusion of disulphonic acids invariably results in the production of resorcinol (meta-dihydroxybenzene), since when dihydric phenols are strongly heated the hydroxy-groups migrate, taking up the meta-position to one another.

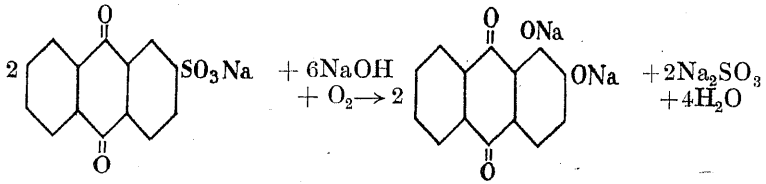
73. Preparation.—Heat cautiously 60 gm. of caustic soda and 3 c.c. of water in a nickel crucible until the temperature reaches 280° C. The thermometer, which is used for stirring the fused mass, must be protected by an outer casing of glass tube, closed at the lower end. Slowly add 20 gm. of powdered β-naphthalene sodium sulphonate (paragraphs **207**, **208**), and then increase the temperature gradually to 320° C., and maintain at this point for ten minutes. Pour the melt on to a clean sand tray. Pulverise the cold mass, dissolve in water, decant the liquid, and acidify carefully with strong hydrochloric acid. When cold, filter the precipitated naphthol, wash, and recrystallise from hot water or from very dilute alcohol. Yield, 10 gm. α-Naphthol may be prepared in a precisely similar manner from the corresponding sulphonic acid.

β-Naphthol crystallises in colourless leaflets, which are soluble in solutions of caustic alkalies. M.P. = 122° C.; B.P. 285–286° C. For tests, see paragraph **288**.

PREPARATION 20. **ALIZARINE,** 

74. Reaction.—By the alkaline fusion of sodium anthraquinone monosulphonate in the presence of an oxidising agent, not only is

the sulphonic group replaced by hydroxyl, but a second phenolic group is introduced by oxidation, thus—



Sodium alizarate

The preparation is of great commercial importance.

75. Preparation.—Place in an autoclave (Fig. 26, page 104), or in an iron pipe, one end of which is closed and the other end fitted with a screw cap, a mixture of 15 gm. of sodium anthraquinone monosulphonate, 45 gm. of sodium hydroxide dissolved in 25 c.c. of water and 4 gm. of finely powdered potassium chlorate. Heat for five hours to a temperature of 190–200° C. Extract the cooled melt several times with boiling water and acidify the hot solution with concentrated hydrochloric acid. Filter off the precipitated alizarine from the cold solution, wash with cold water, and crystallise from glacial acetic acid or from alcohol. Yield, 10 gm.

Alizarine is an orange crystalline solid, soluble in alkalies, giving purple solutions. M.P. 289° C., but sublimes without decomposition at 200°. For tests, see paragraph **291**.

Preparation 21. **PHENOL,** C_6H_5OH.

76. Reaction.—Phenols may be prepared indirectly from aromatic primary amines, by warming the aqueous solutions of the diazonium salts, obtained by diazotisation.

$$C_6H_5N = NCl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

To obtain a good yield, and to avoid contamination with products formed by side reactions, it is essential (i.) to make sure that the amine has been completely diazotised, and (ii.) that no excess of nitrous acid remains in the solution. In practice, therefore, the slight excess of nitrous acid used to complete the diazotisation is destroyed with urea before warming the solution of the diazonium salt.

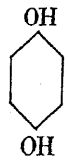
$$CO(NH_2) + 2HNO_2 \rightarrow CO_2 + 3H_2O + 2N_2$$

77. Preparation.—Diazotise 20 gm. of aniline dissolved in 50 c.c. of hydrochloric acid and 150 c.c. of water as described in preparation of benzene (paragraph **39**). To the cold solution obtained, add

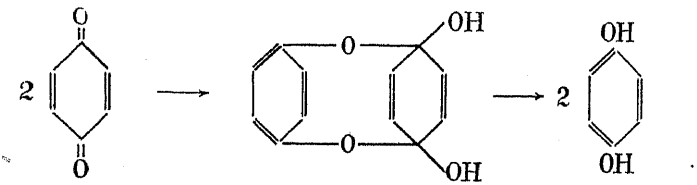
2 gm. of urea, and then warm on the water bath to 50° for half an hour. Steam-distil the mixture to remove the phenol. Saturate the distillate with salt and extract three times with ether. Dry the ethereal solution with freshly fused sodium sulphate. Distil off the ether through a water condenser and then the phenol through a small air condenser, collecting between 180–185° C. Yield, 15 gm.

Phenol is a colourless crystalline solid, with characteristic odour, deliquescent, soluble in about 15 parts of cold water, and very easily soluble in alcohol and ether. M.P. 42·5°; B.P. 183°. For tests, see paragraph **288**.

PREPARATION 22. **QUINOL,**



78. Reaction.—The reduction of the true quinones may be readily brought about by sulphurous acid, as well as by other reducing agents. Intermediate products—the quinhydrones—are first obtained.



Quinone (Coloured quinoid form) — Quinhydrone — Quinol (Colourless benzoid form)

79. Preparation.—Finely powder 15 gm. of quinone (paragraph **99**), and suspend in 200 c.c. of water. Saturate the liquid with gaseous sulphur dioxide and leave it for one hour. Again saturate the solution with sulphur dioxide and leave it for several hours. Extract the solution three times with ether. Distil off the ether, and recrystallise the residue from water after boiling with animal charcoal. Yield, 12 gm.

Quinol (**Hydroquinone**) occurs in colourless leaflets, M.P. 169°, which sublime unchanged. Easily soluble in hot water, slightly soluble in cold water, and easily soluble in alcohol and ether. For tests, see paragraph **288**.

ALDEHYDES

80. Aldehydes may be prepared by the following general methods :—

(i.) *The oxidation of primary alcohols*, usually by means of aqueous potassium dichromate and dilute sulphuric acid (see preparation of acetaldehyde, paragraphs **82, 83**).

(ii.) *The oxidation of side chains in aromatic hydrocarbons.*— Commercially a number of oxidising agents, such as cerium dioxide, persulphates, chromic acid and ozone, are used in this way. It is usually necessary to protect the aldehyde group from further oxidation, at the moment of its formation, by carrying out the reaction in acetic anhydride solution containing sulphuric acid, when the aldehyde is at once converted into the diacetyl derivative. Indirect oxidation is effected by halogenation of the side chain, and then boiling the dichlor-derivative with alkalies or with chalk and water.

$$C_6H_5 . CHCl_2 + 2H_2O \rightarrow C_6H_5 . CH(OH)_2 + 2HCl$$
$$\rightarrow C_6H_5 . CHO + H_2O$$

(see preparation of benzaldehyde, paragraphs **84, 85**, and also paragraphs **45, 46**).

(iii.) *The reduction of carboxylic acids*, either with sodium amalgam and boric acid, or by the dry distillation of the calcium salt with calcium formate. Ketones are produced in a similar way by the dry distillation of the calcium salts *alone* (see preparation of acetone, paragraphs **90, 91**).

$$(CH_3 . COO)_2Ca + (H . COO)_2Ca \rightarrow 2CaCO_3 + 2CH_3 . CHO$$

(iv.) *The replacement of a hydrogen atom in the aromatic nucleus by* — CHO by Reimer's reaction, in which phenols are treated with chloroform and caustic soda solution (see salicylaldehyde, paragraphs **86, 87**).

81. Aldehydes may be purified or isolated by converting them into crystalline derivatives, such as those formed with ammonia, sodium bisulphite, semicarbazide, hydroxylamine and phenylhydrazine, the latter usually being employed in the case of the carbohydrates. These derivatives are of the greatest importance in the identification of aldehydes and ketones (see preparations : acetoxime

(paragraphs **101, 102**); benzaldoxime (**103–105**); benzophenone semicarbazone (**108, 109**); benzaldehyde phenylhydrazone (**110, 111**); and glucosazone (**112, 113**). See also the purification of aldehyde by the ammonia compound (**83**) and of salicylaldehyde by means of the bisulphite compound (**87**).

PREPARATION 23. **ACETALDEHYDE**, $CH_3 . CHO$.

82. Reaction.—Aldehydes may be produced by the careful oxidation of the primary alcohols. The oxidation may be accomplished by means of dilute chromic acid, or catalytically by passing the vapour of the alcohol and air over finely divided metals, such as copper.

The acetaldehyde, formed according to the reaction,

$$2CH_3 . CH_2OH + O_2 \rightarrow 2CH_3 . C\begin{matrix}H\\ \diagup\\ \diagdown\\ O\end{matrix} + 2H_2O$$

is then separated by means of its ammonia compound—

$$CH_3 . C\begin{matrix}H\\ \diagup\\ \diagdown\\ O\end{matrix} + NH_3 \rightarrow CH_3 . C\begin{matrix}H\\ \diagup\\ -OH\\ \diagdown\\ NH_2\end{matrix}$$

and the pure aldehyde obtained from this by distillation with dilute acid :

$$2CH_3 . C\begin{matrix}H\\ \diagup\\ -OH\\ \diagdown\\ NH_2\end{matrix} + H_2SO_4 \rightarrow 2CH_3 . C\begin{matrix}H\\ \diagup\\ \diagdown\\ O\end{matrix} + (NH_4)_2SO_4$$

83. Preparation.—Place a mixture of 65 c.c. of concentrated sulphuric acid and 200 c.c. of water in a 1500 c.c. round-bottomed flask, fitted with a tap funnel. Attach an efficient condenser, which leads directly, by means of an adapter, into a receiver surrounded by ice-water. Place the flask on a sand bath, and heat to boiling. Turn out the flame and run in slowly a solution of 200 gm. of sodium dichromate in 200 c.c. of water and 120 c.c. of absolute alcohol. This solution should be added at such a rate that the heat generated causes the mixture to boil briskly. Heat the liquid on the sand bath for fifteen minutes after the whole of the liquid has been added. The distillate contains water, alcohol, aldehyde and acetal.

Transfer the distillate to a flask placed on a water bath and redistil slowly through a sloping reflux condenser (Fig. 24), and collect the aldehyde in 100 c.c. of *dry* ether.

Maintain the water in the condenser at 30° C., so as to condense

the water and alcohol, but not the aldehyde, and surround the receiver with crushed ice.

Saturate the ethereal solution thus obtained with *dry* ammonia gas and allow it to stand for two hours. Filter off the crystalline aldehyde-ammonia by means of a Buchner funnel, wash with dry ether, and press between filter paper. Yield, 35 gm.

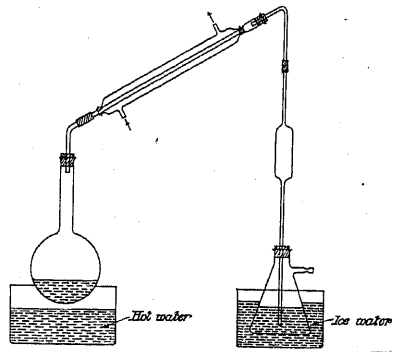


FIG. 24.—Preparation of Acetaldehyde.

To prepare aldehyde from the aldehyde-ammonia place 15 gm. of the aldehyde-ammonia in a round-bottomed flask and add 10 c.c. of water and a cold mixture of 10 c.c. of strong sulphuric acid in 30 c.c. of water. Connect the flask with a water condenser and adapter, heat on a water bath, and collect the aldehyde in a receiver immersed in a mixture of crushed ice and salt.

Acetaldehyde is a mobile, colourless liquid, miscible with water, alcohol and ether. B.P. 21° C.; $\Delta = 0{\cdot}8056$ (°/4). For tests, see paragraph **274**.

Aldehyde-ammonia is a colourless, crystalline solid, easily soluble in water, with difficulty in ether. Melts at 95° and distils at about that temperature with partial decomposition. Alkaline reaction in solution. For tests, see paragraph **326**.

PREPARATION 24. **BENZALDEHYDE,** $C_6H_5 . CHO$.

84. Reaction.—Aldehydes may be obtained from dihalogen compounds of the type $R . CHCl_2$ by treatment with alkali, or with water in the presence of a catalyst such as finely divided iron.

$$\underset{\text{Benzal chloride}}{C_6H_5 . CHCl_2} + Ca(OH)_2 \rightarrow C_6H_5 . CHO + CaCl_2 + H_2O$$

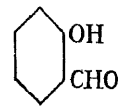
85. Preparation.—Place a mixture of 25 gm. of benzal chloride, 150 c.c. of water and 35 gm. of precipitated chalk, in a round-bottomed flask attached to a reflux condenser. Heat the flask in an oil bath kept at a temperature of about 130°, for three or four hours.

Steam-distil the whole (**8**) until no more benzaldehyde passes over, and extract the distillate with ether. Dehydrate with solid calcium chloride and distil off the ether from a water bath. Distil the residue through a small air condenser in a current of dry carbon

dioxide, collecting the portion that comes over between 178–180°. Keep the benzaldehyde in a well-stoppered container. Yield, 12 gm.

Benzaldehyde (Oil of Bitter Almonds) is a colourless oil, with an odour of bitter almonds. Soluble in 300 parts of water. Highly refractive. Readily oxidises in air to benzoic acid. B.P. = 179·5°; $\Delta = 1{\cdot}050$ (15°/°4). For tests, see paragraph **274**.

PREPARATION 25. **SALICYLALDEHYDE,**



p-**HYDROXYBENZALDEHYDE,**



86. Reaction.—A hydrogen atom present in the nucleus of a phenol can be replaced by an aldehyde group by boiling with chloroform and caustic alkali solution. Substitution takes place in the ortho- and para-positions. This is known as *Reimer's Reaction.*

$$C_6H_4 . H . ONa + CHCl_3 + NaOH \rightarrow C_6H_4 . CHCl_2.ONa + NaCl + H_2O$$

$$C_6H_4 . CHCl_2 . ONa + 2NaOH \rightarrow C_6H_4 . CHO . ONa + 2NaCl + 2H_2O$$

Similarly, by refluxing a phenol with caustic soda and carbon tetrachloride, phenolic carboxylic acids are obtained.

$$C_6H_5ONa + CCl_4 + 5NaOH \rightarrow C_6H_4(ONa)COONa + 4NaCl + 3H_2O$$

87. Preparation.—Place 80 gm. of caustic soda in a round-bottomed flask, and dissolve it in 100 c.c. of water, then add 35 gm. of phenol. By means of a doubly bored cork insert a thermometer so that the bulb is immersed in the liquid, and connect the flask with an efficient reflux condenser. Gradually add, in small instalments, 40 c.c. of chloroform through the condenser, shake on each addition and maintain the reaction mixture at 60–65°, by cooling or by warming, as may be necessary. The time taken for this part of the synthesis should be about two hours.

Steam-distil the contents of the flask so as to remove the excess

of chloroform. Allow to cool and acidify carefully with dilute sulphuric acid. Steam-distil again until no more oil passes over. The salicylaldehyde distils, leaving the non-volatile para-isomer in the flask.

Extract the distillate with ether, and then distil off the ether. The residue contains some unchanged phenol together with the salicylaldehyde. Shake this residue thoroughly with 100 c.c. of a saturated solution of sodium bisulphite, meanwhile stirring and scratching with a glass rod. Shake occasionally, and after an hour filter off the crystalline product with suction; wash three times with alcohol and once with ether to remove phenol. Warm the crystals with dilute sulphuric acid to free the aldehyde from the additive compound. Cool, extract with ether, and dehydrate with anhydrous calcium chloride. Remove the ether by distillation over a water bath, and distil the salicylaldehyde through an air condenser, collecting the portion boiling between 196–197° C. Yield, 14 gm.

The non-volatile para-hydroxybenzaldehyde which remained in the flask after steam distillation, together with resinous compounds, may now be separated. For this purpose filter the contents of the flask whilst hot, and saturate the filtrate with salt. When cold extract the liquid with ether, distil off the ether, and crystallise the residue from hot water containing sulphurous acid. Yield, 3 gm.

Salicylaldehyde is a colourless, fragrant oil, steam-volatile; soluble in water, miscible with alcohol and ether. B.P. 196·5°; $\Delta = 1{\cdot}173$ (13°/4°). For tests, see paragraph **274**.

p-**Hydroxybenzaldehyde** crystallises in colourless needles, non-volatile in steam. Readily soluble in hot water, alcohol and ether. M.P. = 115–116°. For tests, see paragraph **273**.

KETONES AND QUINONES

88. Ketones may be prepared by the following general methods:—

(i.) *The distillation of the barium or calcium salts of the carboxylic acids*, preferably under reduced pressure, see preparation of acetone (**90, 91**).

(ii.) *The oxidation of secondary alcohols* by means of such agents as aqueous chromic acid, nitric acid, or the halogens, or catalytically in the presence of finely divided metals such as copper, see preparation of benzil (**92, 93**).

(iii.) *The oxidation of the diarylmethane compounds*, usually with chromic acid. Compounds of the type of diphenylmethane are readily oxidised to the corresponding ketones.

$$C_6H_5 . CH_2 . C_6H_5 + O_2 \rightarrow C_6H_5 . CO . C_6H_5 + H_2O$$

(iv.) *The Friedel and Craft synthesis*, by the action of anhydrous aluminium chloride on an aromatic compound and an acid chloride, see preparation of acetophenone (**94, 95**).

(v.) *The benzoin condensation*, by the action of potassium cyanide on aromatic aldehydes.

$$2C_6H_5 . CHO \xrightarrow{KCN} \underset{\text{Benzoin}}{C_6H_5 . CHOH . CO . C_6H_5}$$

see preparation of benzoin (**62, 63**).

(vi.) *The ketonic hydrolysis of the acetoacetic esters*, by the action of dilute aqueous alkalies. This is of great importance for the synthetical preparation of the more complex ketones (see paragraph **140**).

89. Quinones are obtained by the following methods:—

(i.) *The oxidation of hydrocarbons* of the naphthalene and anthracene series, with chromic acid, see preparation of anthraquinone (**96, 97**).

(ii.) *The oxidation of primary amines and of phenols* in the benzene series, see preparation of quinone (**98, 99**).

PREPARATION 26. **ACETONE**, $CH_3 . CO . CH_3$.

90. Reaction.—The dry distillation of the calcium, or better, the barium salts, of the carboxylic acids gives rise to the

ketones. Better yields are obtained by distilling under reduced pressure.

$$(CH_3COO)_2Ca \rightarrow CH_3 . CO . CH_3 + CaCO_3$$

The bulk of the acetone of commerce is manufactured in this way, although some is produced by fermentation processes.

Mixed ketones may be obtained by distilling an intimate mixture of the salts of two different acids.

91. Preparation.—Place in a hard glass tube, fitted with a water condenser, 200 gm. of *anhydrous* barium acetate and heat until no more liquid distils over. Treat the distillate with three times its own volume of a saturated solution of sodium bisulphite, place in a stoppered bottle, and agitate on a mechanical shaker for several hours. Filter off the crystalline product, and gently distil with an excess of sodium carbonate solution, using a water bath. Collect the distillate up to a temperature of 65° C. Dehydrate the product with anhydrous calcium chloride, redistil and collect at a temperature of from 56–57° C.

Acetone is a mobile, colourless liquid, with a pleasant odour, miscible with water, alcohol and ether. B.P. = 56·5°; Δ = 0·819 (0°/4°). For tests, see paragraph **292**.

PREPARATION 27. **BENZIL,** $C_6H_5 . CO . CO . C_6H_5$.

92. Reaction.—Whereas the oxidation of primary alcohols yields aldehydes, the oxidation of secondary alcohols readily yields ketones, and the oxidation of the benzoins yields the α-diketones, thus—

$$2C_6H_5 . CHOH . CO . C_6H_5 + O_2 \rightarrow 2C_6H_5 . CO . CO . C_6H_5 + 2H_2O.$$

Benzil is the most common of the α-diketones. It is characteristic of this class of substances that they all possess a yellow colour.

93. Preparation.—Heat in an open flask, on a rapidly boiling water bath, a mixture of 14 gm. of benzoin and 20 c.c. of pure nitric acid (Δ = 1·42). After two hours heating pour the resultant oil into water, filter off the crystalline product, wash with water, and recrystallise from alcohol. Yield, 11 gm.

Benzil crystallises in pale yellow needles. It is insoluble in water and easily soluble in alcohol and ether. M.P. 95°; B.P. 346°. For tests, see paragraph **291**.

PREPARATION 28. **ACETOPHENONE,** $CH_3 . CO . C_6H_5$.

94. Reaction.—Friedel and Craft have shown that the condensation of aromatic compounds and acid chlorides takes place under the influence of anhydrous aluminium chloride.

$$C_6H_6 + CH_3 . CO . Cl \rightarrow C_6H_5 . CO . CH_3 + HCl$$

Also in a similar way the hydrocarbons can be synthesised by the condensation of a hydrocarbon and an alkyl halide, see preparation of triphenylmethane (paragraphs **34, 35**).

If a substituted hydrocarbon is used, then the ketone group enters the para-position; or, if this is already occupied, the ortho-position. Phosgene, and other acid chlorides derived from dibasic acids, will react with two molecules of the aromatic hydrocarbon.

$$2C_6H_6 + CO . Cl_2 \rightarrow C_6H_5 . CO . C_6H_5 + 2HCl$$

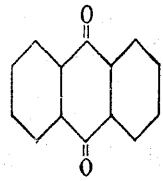
Michler's ketone (*p.p*-dimethylaminobenzophenone) is obtained similarly by the action of phosgene on dimethylaniline.

$$2C_6H_5N(CH_3)_2 + CO . Cl_2 \rightarrow \begin{matrix}(CH_3)_2N . C_6H_4 \\ (CH_3)_2 . N . C_6H_4\end{matrix}\!\!>C = O + 2HCl.$$

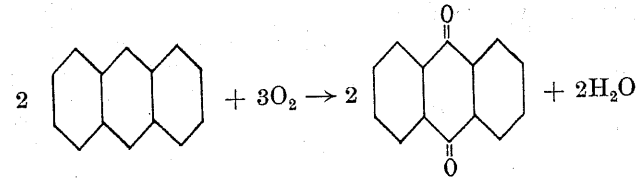
95. Preparation.—In a round-bottomed flask, fitted with a reflux condenser and with a tap funnel, place 50 gm. of resublimed anhydrous aluminium chloride (*Note*) and immediately cover it with 40 c.c. of dry benzene. Immerse the flask in ice-water and run in, drop by drop, 35 gm. of redistilled acetyl chloride. A vigorous evolution of hydrochloric acid will take place. After allowing the mixture to stand for an hour, pour the mixture into 250 c.c. of crushed ice and water. Extract the liquid in a separating funnel once with benzene, and wash the benzene solution once with caustic soda, and then twice with water. Dehydrate the benzene solution with anhydrous calcium chloride and distil off the benzene through a water condenser. Distil the residue left in the flask through a short air condenser, collecting the distillate between the temperatures of 195° and 205° C. Yield, 25 gm.

Acetophenone is a crystalline solid of characteristic and pleasant odour. Insoluble in water. M.P. = 20·5° C.; B.P. = 202° C. For tests, see paragraph **291**.

NOTE.—As the whole efficiency of the experiment depends on the quality of the aluminium chloride, this must either be freshly prepared or else resublimed from a small retort.

PREPARATION 29. **ANTHRAQUINONE,** 

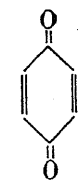
96. Reaction.—Hydrocarbons of the naphthalene and anthracene series may be directly oxidised to quinones by the use of chromic acid. Either a mixture of sodium dichromate and sulphuric acid, or of chromic anhydride in glacial acetic acid, may be used.



Commercial specimens of the crude hydrocarbons must be purified by recrystallisation before oxidation to quinones.

97. Preparation.—Dissolve 10 gm. of pure anthracene in 120 c.c. of glacial acetic acid, and place in a 500 c.c. flask, fitted with a reflux condenser. Heat up to boiling-point and slowly add a solution of 20 gm. of chromic anhydride dissolved in 15 c.c. of water and 75 c.c. of glacial acetic acid, the liquid being kept boiling during the addition. Reflux for a further half hour after the chromic acid has been added. Cool and pour the solution into 500 c.c. of water. Filter off the precipitated anthraquinone and wash well with hot water on a Buchner funnel. Dry the product in the steam oven and purify it by sublimation, as described in paragraph **5**. The anthraquinone may also be purified by crystallisation from glacial acetic acid. Yield, 10 gm.

Anthraquinone sublimes in pale yellow needles. It is soluble in 45 parts of hot alcohol. M.P. 275°; B.P. 380°. For tests, see paragraph **291**.

PREPARATION 30. **QUINONE,** 

98. Reaction.—In the benzene series, primary amines, such as aniline, are oxidised to para-quinones by means of chromic acid,

with simultaneous elimination of the amino-group. Para-diamines are even more readily oxidised. In a similar manner both ortho- and para-quinones are obtained from diamines, amino-phenols and dihydric phenols. Oxidation of ortho-compounds, such as pyrocatechol, to the corresponding ortho-quinones is difficult, and is only possible if all moisture is excluded. It is usually effected by the action of dry silver oxide on the phenol dissolved in anhydrous ether.

99. Preparation.—Dissolve 25 gm. of aniline in a mixture of 600 c.c. of water and 120 c.c. of concentrated sulphuric acid. Surround this solution with crushed ice and stir it by means of a mechanical stirrer. Dissolve 75 gm. of sodium dichromate in 250 c.c. of water and from a tap funnel cautiously add one-third of this solution to the ice-cold aniline sulphate, not allowing the temperature to exceed 10° C. Allow to stand for eight hours and then slowly add the remainder of the dichromate, keeping the solution cool and stirring continuously. After standing for another three hours, extract the liquid with 250 c.c. of ether, by *gentle shaking*, since vigorous shaking produces an emulsion. Distil off the ether, and again extract the solution with the recovered ether. Repeat this a third time. Pass a rapid current of steam over the crystalline quinone obtained by evaporation of the ethereal extracts. The quinone sublimes in the steam and condenses in the form of golden yellow needles in the receiver. Filter and dry in an *ordinary* desiccator. Yield, 12 gm.

Quinone crystallises in golden yellow, monoclinic prisms, easily soluble in alcohol and ether. Soluble in alkalies. Sublimes easily. Possesses a peculiar sharp irritating odour. M.P. 115·7° C. For tests, see paragraph **291.**

OXIMES

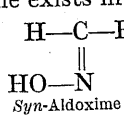
100. Oximes are readily formed by the action of hydroxylamine on aldehydes or ketones :

$$R \cdot CHO + H_2NOH \rightarrow \underset{\text{Aldoxime}}{R \cdot CH : NOH} + H_2O$$

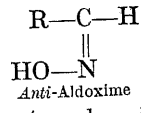
$$R \cdot R \cdot C = O + H_2NOH \rightarrow \underset{\text{Ketoxime}}{R \cdot R \cdot C : NOH} + H_2O$$

On hydrolysis they pass back again into the corresponding aldehyde or ketone.

The oximes are capable of exhibiting geometrical isomerism, thus aldoxime exists in the two forms :



Syn-Aldoxime



Anti-Aldoxime

Since the monoximes of the α-diketones (*e.g.*, benzil) are identical with the *iso-nitroso ketones*, these are usually best obtained by the action of nitrous acid on ketones containing the group —CO—CH_2, thus :

$$CH_3 \cdot CO \cdot CH_2CH_3 + O : NOH \rightarrow CH_3 \cdot \underset{\underset{O}{\|}}{C}—\underset{\underset{NOH}{\|}}{C} \cdot CH_3$$

See preparation of camphor quinone oxime (**106, 107**).

It should also be noted that para-nitrosophenols are identical with the quinone monoximes. These may be formed by the direct action of nitrous acid on phenols (see paragraphs **168, 169**). The oxime and the nitrosophenol must be regarded as tautomeric.



PREPARATION 31. **ACETONEOXIME,** $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C = NOH.$

101. Reaction.—The oximes are prepared by the interaction of hydroxylamine hydrochloride on the aldehyde or ketone, in the

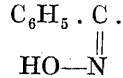
presence of a basic substance such as caustic soda or barium carbonate (see paragraph **100**).

102. Preparation.—Shake well together in a small-corked flask a mixture of 5 gm. of hydroxylamine hydrochloride dissolved in 10 c.c. of water, 4 gm. of caustic potash dissolved in 10 c.c. of water, and 8 c.c. of acetone. Leave for twenty-four hours, and filter off the crystallised oxime. Extract the liquid with 25 c.c. of ether, and dissolve the solid product in the same ether. Dehydrate with anhydrous calcium chloride and distil off the bulk of the ether. Pour into a small crystallising dish and allow the residual ether to evaporate in the air. Dry on a porous plate. Yield, 6 gm. The product may be recrystallised from dry heptane.

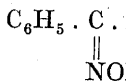
Acetoneoxime (Acetoxime) crystallises in colourless needles, with a faint odour. Very soluble in water, alcohol and ether. M.P. = 59°; B.P. = 135°. For tests, see paragraph **334**.

PREPARATION 32. **α- and β-BENZALDOXIMES,** $C_6H_5CH : NOH$.

103. Reaction.—The two benzaldoximes are stereoisomers, exhibiting geometric isomerism similar to fumaric and maleic acids. Their nature was demonstrated by Hantzsch and Werner in 1890.



α-Benzaldoxime



β-Benzaldoxime

By the action of dehydrating agents such as acetic anhydrides, the β-compound yields benzonitrile, whilst the α-compound does not do so.

104. Preparation of α-Benzaldoxime.—To a mixture of 25 gm. of benzaldehyde and 17 gm. of caustic soda dissolved in 50 c.c. of water, add slowly, with continuous shaking, 18 gm. of hydroxylamine hydrochloride. Continue to shake until the benzaldehyde dissolves. Dilute the whole with 100 c.c. of water and pass carbon dioxide through the liquid until saturated. Extract the α-benzaldoxime with ether, dehydrate with anhydrous sodium sulphate and distil off the ether. The impure product is added to a solution of sodium ethylate, obtained by dissolving 6 gm. of sodium in 70 gm. of absolute alcohol, and the solid sodium salt filtered off and washed with sodium ethylate solution in which the β-compound, which is present in small quantity, is soluble. The residue is dissolved in water, the free oxime liberated with carbon dioxide

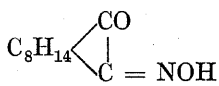
and extracted with ether. The ethereal solution is thoroughly dried with anhydrous calcium chloride and the ether distilled off. The oxime is cooled with powdered ice and salt, with scratching, in order to cause it to crystallise. Yield, 14 gm.

105. Preparation of β-Benzaldoxime.—Prepare 250 c.c. of pure anhydrous ether (see paragraph **33**). Dissolve 7 gm. of the α-compound in 40 c.c. of the purified ether and pass in dry hydrochloric acid gas, taking care not to allow the tube to become choked. Filter the crystalline β-oxime hydrochloride, wash with dry ether and cover with a layer of ether in a conical flask. Add a concentrated solution of sodium carbonate until effervescence ceases. Shake gently and separate off the ethereal layer. Dehydrate with anhydrous sodium sulphate and distil off the ether rapidly *under reduced pressure* (paragraph **10**). Dry the crystalline residue on a porous plate. Yield, 6 gm.

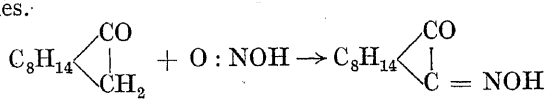
α-Benzaldoxime (anti-) crystallises in colourless needles. Soluble in alcohol and ether, but with difficulty in water. M.P. 33°; B.P. 118–119° (10 mm.). For tests, see paragraph **334.**

β-Benzaldoxime (syn-) crystallises in thin, lustrous needles or tablets. Difficultly soluble in benzene (unlike α-compound). M.P. 129°. For tests, see paragraph **334.**

PREPARATION 33. CAMPHOR QUINONE MONOXIME,



106. Reaction.—By the action of nitrous acid on ketones containing the —CO—CH_2— group the *iso*-nitroso compounds are obtained. These are identical with the monoximes of the α-diketones.



107. Preparation.—Dissolve 25 gm. of camphor in 150 c.c. of *dry* ether contained in a 500-c.c. round flask. Add 4 gm. of sodium wire and cool the flask in ice. Add in small quantities 20 gm. of amyl nitrite, vigorously shaking and keeping cool. Leave for one hour and then pour into 500 c.c. of ice and water, taking care if there is any unchanged sodium. Separate and extract the aqueous solution twice with ether to remove unchanged camphor. Bubble air through the aqueous solution for fifteen minutes to remove ether and just acidify with dilute acetic acid to decompose the

sodium salt. Filter off the precipitated oxime and recrystallise it from heptane. Yield, 12 gm.

Camphor Quinone Monoxime (*iso*-nitrosocamphor) crystallises in colourless needles. M.P. 153° C. For tests, see paragraph **334**.

PREPARATION 34. **BENZOPHENONE-SEMICARBAZONE,**

$$(C_6H_5)_2C = N . NH \diagdown \begin{matrix} \\ NH_2 \end{matrix} \diagup C = O$$

108. Reaction.—The semicarbazones of the aldehydes and ketones are well-crystallised solids that are of the utmost value for purposes of identification. They are prepared by the addition of the aldehyde or ketone to a solution of semicarbazide in alcohol and water at a moderate temperature. On cooling, or on pouring into water, the crystalline derivative separates:

$$R . C \begin{matrix} H \\ \diagdown\!\!\diagup \\ O \end{matrix} + \begin{matrix} NH_2 \\ \diagdown \\ H_2N . NH \end{matrix} \!\!\diagup C = O \rightarrow R . C \begin{matrix} H\ NH_2 \\ \diagdown\!\!\diagup \\ N . NH \end{matrix} \!\!\diagup C = O + H_2O$$

A slight excess of semicarbazide should be used.

109. Preparation.—Dissolve 2 gm. of semicarbazide hydrochloride and 3 gm. of crystallised sodium acetate in the smallest possible quantity of warm water. Add 3 gm. of benzophenone and just sufficient hot alcohol to form a clear solution. Reflux gently over a water bath for one hour, and pour into water. Filter off the precipitated semicarbazone, wash with very dilute alcohol, and recrystallise from *pure* acetone or from alcohol. Yield, 3·5 gm.

Benzophenone-semicarbazone crystallises in colourless needles from alcohol. It is soluble in hot alcohol and in acetone. M.P. 165° C. For tests, see paragraph **334**.

PREPARATION 35. **BENZALDEHYDE-PHENYLHYDRAZONE,**

$$C_6H_5C \begin{matrix} H \\ \diagdown\!\!\diagup \\ N . NH . C_6H_5 \end{matrix}$$

110. Reaction.—Hydrazine and its derivatives form insoluble but easily crystallised derivatives with aldehydes and ketones. These compounds are of great importance in their identification. The derivatives of phenylhydrazine, para-bromphenylhydrazine and benzylphenylhydrazine are those usually prepared.

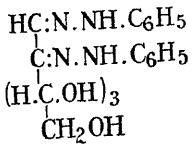
$$CH_3 . C \begin{matrix} H \\ \diagdown\!\!\diagup \\ O \end{matrix} + H_2N . NH . C_6H_5 \rightarrow CH_3 . C \begin{matrix} H \\ \diagdown\!\!\diagup \\ N . NH . C_6H_5 \end{matrix} + H_2O$$

The free base is dissolved in dilute acetic acid solution, or sodium acetate is added in excess to the aqueous solution of the hydrochloride, and the aldehyde or ketone added. In most cases the derivative forms at the ordinary temperature.

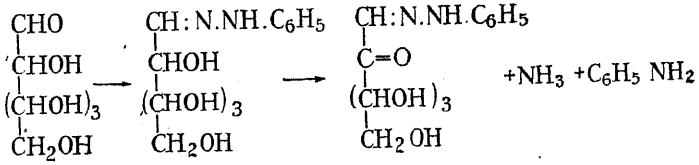
111. Preparation.—Dissolve 4 c.c. of phenylhydrazine in a mixture of 3 c.c. of glacial acetic acid and 20 c.c. of water. Add 2 gm. of benzaldehyde and shake vigorously. Leave for two hours, shaking occasionally. Filter off the precipitated hydrazone and wash first with a little dilute acetic acid and then with water. Finally recrystallise from alcohol. Yield, 3 gm.

Benzaldehyde-phenylhydrazone (α form) crystallises in monoclinic prisms from dilute alcohol. Easily soluble in hot alcohol, acetone and benzene; but only with difficulty in ether. Distils unchanged. M.P. 155–156°. For tests, see paragraph **334**.

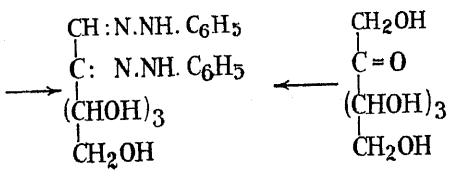
PREPARATION 36. **GLUCOSAZONE,**



112. Reaction.—The aldoses and ketoses readily form phenylhydrazones, which are usually very soluble. If the phenylhydrazine is used in excess it acts as an oxidising agent, forming, in the case of the aldoses, a —CO group from the α—CHOH group, and this —CO group again reacts with the phenylhydrazine to give a bi-phenylhydrazone, or an *osazone*.



Glucose



Osazone Fructose

The ketoses react in a similar way; thus fructose gives rise to the same osazone as glucose. By means of the osazones, aldoses may be converted into ketoses.

The colours, crystalline forms and melting-points of the osazones afford satisfactory means of identifying the sugars.

113. Preparation.—Dissolve 4 gm. of phenylhydrazine hydrochloride and 6 gm. of sodium acetate in 30 c.c. of water. Add to this cold solution 2 gm. of glucose dissolved in 10 c.c. of water. Warm on the water bath, when the osazone will begin to separate at the end of a few minutes and the reaction will be complete in about an hour. Filter off the crystals which separate, wash with a little water, and recrystallise from 50 per cent. alcohol. Dry the crystals on a porous plate. Yield, 4 gm.

Glucosazone, identical with the osazones of fructose and mannose, crystallises in yellow needles. M.P. = 204° C.

CARBOXYLIC ACIDS

114. The carboxylic acids may be prepared by the following general methods :—

(i.) *The hydrolysis of trihalogen compounds* in which the halogen atoms are all attached to the same carbon atom :

$$CHCl_3 + 3KOH \rightarrow H \,.\, COOH + 3KCl + H_2O$$

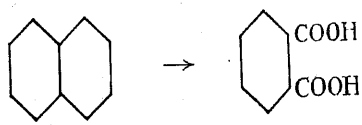
For the preparation of benzoic acid by the hydrolysis of benzotrichloride, see paragraph **45.**

(ii.) *The oxidation of alcohols, aldehydes and ketones.*—Primary alcohols and aldehydes give rise to acids containing the same number of carbon atoms :

$$2CH_3 \,.\, CHO + O_2 \rightarrow 2CH_3COOH$$

The vigorous oxidation of many compounds leads to the production of fairly simple acids, such as oxalic acid, and carbon dioxide (see oxalic acid, paragraphs **115, 116**).

(iii.) *By the oxidation of side chains in aromatic compounds* carboxylic acids are produced. Chromic acid, nitric acid, and alkaline permanganate are usually employed.



Thus naphthalene gives rise to phthalic acid (see *p*-aminobenzoic acid, paragraphs **117, 118**).

(iv.) *The hydrolysis of nitriles* with aqueous alkalies :

$$CH_3CN + 2H_2O \rightarrow CH_3COOH + NH_3$$

(see malonic ester, paragraphs **119, 120**).

(v.) *The action of carbon dioxide on the Grignard reagent :*

$$CH_3MgBr + CO_2 \rightarrow CH_3C\begin{matrix}O\\ \diagdown\\ \diagup\\ OMgBr\end{matrix} \xrightarrow{H_2O} CH_3COOH$$

(vi.) *By the action of carbon dioxide on the phenates*, phenolic acids are produced (**Kolbe's synthesis**) :

$$C_6H_5ONa + CO_2 \rightarrow C_6H_4 \,.\, (OH) \,.\, COONa$$

(see salicylic acid, paragraphs **121, 122**).

(vii.) *From aldehydes and ketones by condensation.*—By the action of dehydrating agents, such as the acid anhydrides, on aromatic aldehydes and sodium salts of aliphatic acids of the type $-CH_2 . COOH$, aromatic unsaturated acids are produced (**Perkin's synthesis**):

$$C_6H_5 . CHO + CH_3 . COONa \rightarrow \underset{\text{Sodium cinnamate}}{C_6H_5CH : CH . COONa} + H_2O$$

Similarly, by the action of sodium on aromatic aldehydes and esters, derived from acids of the type $-CH_2COOH$, esters of unsaturated acids are produced (**Claisen's synthesis**):

$$C_6H_5CHO + CH_3COOCH_3 \rightarrow \underset{\text{Methyl cinnamate}}{C_6H_5 . CH : CHCOOCH_3} + H_2O$$

(see cinnamic acid, paragraphs **123, 124,** and methyl cinnamate, paragraphs **125, 126**).

(viii.) *The "acid hydrolysis" of the alkyl acetoacetic esters and malonic esters.*—Synthetic acids of value may be prepared in this way. Thus, by the action of the alkyl iodides on sodium aceto-acetic ester, the alkyl acetoacetic esters are obtained which, when hydrolysed with alcoholic potash, give rise to acids. Aqueous, dilute alkalies give "ketonic hydrolysis."

$$CH_3 . CO . \underset{\underset{Na}{|}}{CH} . COOC_2H_5 \xrightarrow{R.I.} CH_3 . CO . \underset{\underset{R}{|}}{CH} . COOC_2H_5 \xrightarrow{Na}$$

$$CH_3 . CO . \underset{\underset{Na}{|}}{CR} - COOC_2H_5 \xrightarrow{R_1I} CH_3 . CO . C\begin{matrix} R \\ \diagup \\ \diagdown \\ R_1 \end{matrix} - COOC_2H_5 \xrightarrow[\text{conc.}]{KOH}$$

$$CH_3 . COOK + CH . R . R_1 . COOK + C_2H_5 . OH$$

(see acetoacetic ester, paragraphs **138, 139,** and ethyl acetoacetic ester, paragraphs **140–141**).

Preparation 37. **OXALIC ACID,** $\begin{matrix} COOH \\ | \\ COOH \end{matrix}$

115. Reaction.—By the vigorous oxidation of the carbohydrates with nitric acid, oxalic acid is produced. Commercially patents have been taken out for the oxidation of sawdust to oxalic acid by means of nitric acid, and with permanganates. Formerly oxalic acid was obtained by the oxidation of sawdust by fusion with alkalies; it is now obtained by the catalytic decomposition of formates at 360°,

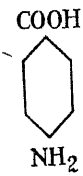
$$2H . COONa \rightarrow H_2 + \begin{matrix} COONa \\ | \\ COONa \end{matrix}$$

the sodium formate being produced by the action of carbon monoxide on caustic soda at 170° C. and at a pressure of seven atmospheres (**Goldschmidt's Process**).

116. Preparation.—Place 150 c.c. of concentrated nitric acid ($\Delta = 1{\cdot}42$), in a large round-bottomed flask and heat to 50° C. Add 0·2 gm. of vanadium pentoxide to act as an oxidation catalyst. Place the flask in the fume cupboard and slowly add 20 gm. of finely powdered cane sugar. When the vigorous reaction has ceased, allow the flask to cool, and leave it for twenty-four hours. Filter off the crystallised oxalic acid by means of a Buchner funnel, containing no filter paper, and recrystallise from as little water as possible. Yield, 15 gm.

Oxalic Acid crystallises in colourless monoclinic prisms containing 2 molecules of water, which are driven off at 100°. The acid is fairly soluble in alcohol and water and slightly soluble in ether. The hydrated crystals melt at 99°. For tests, see paragraph **281.**

PREPARATION 38. ***p*-AMINOBENZOIC ACID,**



117. Reaction.—The oxidation of aromatic side chains is accomplished by the use of such agents as moderately dilute nitric acid, ferricyanides, permanganates or chromic acid.

Ferricyanides can only be used when electronegative groups, such as the nitro-group, are in the ortho-position with respect to the side chain.

Permanganates are usually employed in alkaline solution, and the soluble sodium or potassium salt of the resultant acid filtered from the precipitated manganese dioxide. The filtrate on acidification yields the acid, which crystallises out.

Amino- or phenolic groups, present in the nucleus, must be protected by acetylation before the oxidation of the side chain is commenced. The latter operation should then be carried out in the presence of magnesium sulphate or calcium chloride in order to neutralise the free caustic alkali, which otherwise would split off the protecting group:

$$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3O$$
$$2KOH + MgSO_4 \rightarrow K_2SO_4 + Mg(OH)_2.$$

Vanadium pentoxide is frequently employed as a catalyst.

118. Preparation.—Place, in a large casserole or flask, 25 gm. of acet-para-toluidide (*Note*), 200 c.c. of water and 0·2 gm. of vanadium pentoxide, and heat until just boiling. Add slowly, with heating, a solution of 53 gm. of potassium permanganate and 41 gm. of crystallised magnesium sulphate dissolved in 1,500 c.c. of water, at such a rate that the permanganate is decolorised. Filter the boiling liquid, and *when cold*, add to the filtrate hydrochloric acid until just acid. Filter off the precipitated acetyl-*p*-aminobenzoic acid and wash with a little cold water. Yield, 20 gm.

Hydrolyse 10 gm. of the product by refluxing it with 200 c.c. of dilute hydrochloric acid (4N) for one hour. Filter, and make the cold filtrate just alkaline with caustic soda and then add a slight excess of acetic acid and 30 gm. of salt (NaCl). Filter off the precipitated *p*-aminobenzoic acid and wash with a little cold water. Yield, 7 gm.

NOTE.—Acet-para-toluidide is prepared by the addition of a slight excess of acetic anhydride to 18 gm. of powdered para-toluidine. The crude product may be used directly after one washing with a little dilute caustic soda. See paragraphs **159, 160.**

Acetyl-*p*-aminobenzoic Acid crystallises in needles. It is moderately soluble in alcohol, but is only slightly soluble in water and ether. M.P. = 250° C., with partial decomposition.

***p*-Aminobenzoic Acid** crystallises in odourless needles from alcohol. It is almost insoluble in cold water, but is soluble in acids and alkalies, as it is amphoteric. M.P. = 184° C. For tests, see paragraph **331.**

PREPARATION 39. MALONIC ESTER, $CH_2(COOC_2H_5)_2$

119. Reaction.—Acids are readily obtained by the hydrolysis of nitriles, thus malonic acid is produced from cyanacetic acid :

$$CH_2 . CN . COOH + 2H_2O \rightarrow CH_2(COOH)_2 + NH_3$$

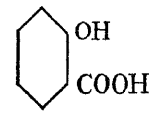
The cyanacetic acid is obtained by the interaction of potassium cyanide and chloracetic acid :

$$CH_2Cl . COOH + KCN \rightarrow CH_2 . CN . COOH + KCl$$

120. Preparation.—Dissolve 25 gm. of chloracetic acid (paragraphs **41, 42**) in 50 c.c. of water contained in a 6-inch porcelain dish. Warm the solution to 50° C. and add powdered potassium carbonate until the evolution of carbon dioxide ceases, and the liquid is neutral. About 20 gm. of the carbonate will be required.

To this solution add 20 gm. of finely powdered potassium cyanide, stirring continuously, and carrying out the operation in a fume chamber. Cautiously heat on a sand bath, with constant stirring, until the temperature reaches 135° C. Allow to cool, stirring continuously, in order to prevent the crude potassium cyanacetate setting to a hard mass. Coarsely powder the product and place it in a round-bottomed flask fitted with a reflux water condenser. Add 20 c.c. of absolute alcohol with shaking; and then, during the course of fifteen minutes, add a cold mixture of 50 c.c. of absolute alcohol and 50 c.c. of strong sulphuric acid. Reflux on the water bath for two hours, whereby simultaneous hydrolysis of the nitrile and esterification of the acid will take place. Well cool and add 100 c.c. of water, with shaking. Filter off any undissolved potassium sulphate and wash this residue with ether. Extract the filtrate three times with fairly large quantities of ether. Well wash the combined ethereal extracts with a saturated solution of sodium carbonate until no longer acid. Dehydrate with freshly fused sodium sulphate and distil off the ether from a water bath. Distil the residue through an air condenser, collecting the fraction between 194–200° C. Yield, 20 gm.

Malonic Ester is a colourless liquid, with a pleasant, aromatic odour. Soluble in alcohol and ether. B.P. = 198°; $\Delta = 1{\cdot}077$ (0°/4°). For tests, see paragraph **286.**

PREPARATION 40. SALICYLIC ACID, 

121. Reaction.—By the action of carbon dioxide on heated anhydrous sodium phenates the oxybenzoic acids are produced:

$$C_6H_5ONa + CO_2 \xrightarrow{110°} \underset{\text{Sodium phenyl carbonate}}{C_6H_5 . O . COONa}$$

$$C_6H_5 . O . COONa + C_6H_5ONa \xrightarrow{200°} \underset{\text{Sodium salicylate}}{C_6H_4.(ONa) . COONa} + C_6H_5OH$$

$$C_6H_4(ONa)COONa + 2HCl \rightarrow C_6H_4(OH)COOH + 2NaCl$$

This is known as **Kolbe's synthesis.** By the action of carbon dioxide on the corresponding potassium phenates the para-oxybenzoic acids are obtained and not the ortho-derivatives. Polyhydric phenols react with great readiness, the oxy-acids being formed by merely heating with aqueous solutions of ammonium carbonate or potassium bicarbonate under pressure.

Commercially salicylic acid is produced by a modification of the above process, known as **Schmitt's synthesis**, in which the phenate is heated in an autoclave to 140° C., whereby it is entirely transformed into sodium salicylate:

$$C_6H_5ONa + CO_2 \rightarrow C_6H_4(OH)COONa$$

The salicylic acid is then liberated by the addition of hydrochloric acid.

122. Preparation.—Dissolve 46 gm. of phenol in a solution of 20 gm. of caustic soda in 25 c.c. of water. Cautiously heat the solution in a well-clamped nickel dish over a naked luminous flame, constantly stirring with a glass rod, until the whole is a dry mass. Powder the mass in a mortar and transfer it to a tubulured retort, almost completely immersed in an oil bath and kept at a temperature of 115° C. At this temperature pass a current of *dry* carbon dioxide over the heated phenate for an hour. The success of the experiment depends on the production of absolutely dry sodium phenate.

Now raise the temperature of the oil bath gradually so that it reaches 200° at the end of four hours, continuing to pass dry carbon dioxide. During this time a considerable amount of phenol distils over to solidify in the neck of the retort, or into a boiling tube which is used as a receiver. Maintain the temperature at 200° for one hour. During the heating process shake the retort occasionally to expose fresh surfaces to the action of the carbon dioxide.

Allow the retort to cool and shake as much of the residual product as possible into a beaker. Nearly fill the retort with water to dissolve out any of the product remaining. Pour the resultant solution on to the mass in the beaker, which will readily dissolve. Acidify this solution with concentrated hydrochloric acid, and when cold filter off the impure salicylic acid that is precipitated. Dissolve the product in water, boil gently with a little animal charcoal, and recrystallise. *N.B.*—Salicylic acid is steam-volatile. Yield, 12 gm.

Salicylic Acid crystallises in white needles, soluble in 500 parts of cold water and in 12 parts of hot water. It is soluble in alcohol and in ether. M.P. 158°. For tests, see paragraph **281.**

PREPARATION 41. CINNAMIC ACID, $C_6H_5 . CH : CH . COOH$.

123. Reaction.—When an aromatic aldehyde reacts with the sodium salt of an aliphatic acid of the type $R—CH_2COOH$, in the presence of an acid anhydride which acts as a condensing agent,

unsaturated carboxylic acids are produced. This is known as **Perkin's synthesis.** The reaction takes place in two stages :

$$C_6H_5 . CHO + CH_3 . COONa \rightarrow \underset{\text{Sodium phenyl } \beta\text{-hydracrylate}}{C_6H_5 . CH(OH) . CH_2 . COONa}$$

$$C_6H_5 . CH(OH) . CH_2 . COONa \rightarrow \underset{\text{Sodium cinnamate}}{C_6H_5 . CH : CH . COONa}$$

In order to avoid mixed products it is advisable to use as the condensing agent the acid anhydride corresponding to the sodium salt used, since, for example, acetic anhydride and sodium propionate would react as follows :—

$$\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>\!O + 2C_2H_5 . COONa \rightleftharpoons \begin{matrix} C_2H_5 . CO \\ C_2H_5 . CO \end{matrix}\!\!>\!O + 2CH_3 . COONa$$

124. Preparation.—Fit a 200-c.c. round-bottomed flask with a moderately wide air condenser, closed at the upper end with a calcium chloride drying tube. Mix in the flask 30 gm. of acetic anhydride and 20 gm. of benzaldehyde, both recently redistilled. Add 10 gm. of freshly prepared, powdered, anhydrous sodium acetate and heat the whole on an oil bath to 180° for twelve hours. Transfer the hot reaction mixture to a large flask, make alkaline with a moderately strong solution of sodium carbonate, and steam distil until no more unchanged benzaldehyde passes over. Filter whilst hot the solution remaining in the flask, cool and acidify with concentrated hydrochloric acid. Filter off the precipitated cinnamic acid when cold, and recrystallise from boiling water. Yield, 18 gm.

Cinnamic Acid (Phenyl Acrylic Acid) crystallises in colourless prisms. It possesses a faint aromatic odour. It is almost insoluble in cold water, but easily soluble in alcohol and ether. M.P. 133° ; B.P. 300°, without decomposition. For tests, see paragraph **281.**

PREPARATION 42. METHYL CINNAMATE, $C_6H_5 . CH : CH . COOCH_3$.

125. Reaction.—By a reaction analogous to Perkin's synthesis, (paragraph **123**), aldehydes may be made to condense with esters, derived from acids of the type R—CH_2COOH, under the influence of condensing agents, such as metallic sodium or acid anhydrides. This is known as **Claisen's synthesis** (see also acetoacetic ester, paragraphs **138, 139**).

$$R . CHO + R' . CH_2 . COOCH_3 \rightarrow R . CH : CR' . COOCH_3 + H_2O$$

126. Preparation.—To 50 c.c. of pure, dry methyl acetate, con-

tained in a round-bottomed flask, cooled externally with powdered ice, add 20 gm. of sodium wire. Slowly add, with shaking, 10 gm. of benzaldehyde. Shake occasionally until all the sodium dissolves and allow to stand for three hours. Add dilute acetic acid until the liquid is acid in reaction and extract with ether. Wash the ethereal extract with sodium carbonate solution, then with water, and dehydrate with solid calcium chloride. Distil off the ether from a water bath and fractionate the residual ester, using an air condenser, collecting the fraction between 260–265° C. The ester solidifies on standing. Yield, 8 gm.

Methyl Cinnamate is a colourless, crystalline solid, soluble in alcohol and ether. M.P. = 36°; B.P. = 260°. For tests, see paragraph **285**.

ACID ANHYDRIDES

127. (i.) **The acid anhydrides derived from dibasic acids** are formed by the elimination of water from two carboxyl groups present in the same molecule:

$$\begin{matrix}CH_2 . COOH \\ | \\ CH_2 . COOH\end{matrix} \rightarrow \begin{matrix}CH_2 . CO \\ | \\ CH_2 . CO\end{matrix}\!\!>\!O + H_2O$$

They are, as a general rule, only formed by those aliphatic acids whose carboxyl groups are separated by not more than three carbon atoms, *i.e.*, acids of the succinic, glutaric and maleic series, and by aromatic *ortho*-dicarboxylic acids, such as phthalic acid. These anhydrides are easily obtained by heating the acid either alone or with a dehydrating agent, such as sulphuric acid or acetic anhydride.

(ii.) **The acid anhydrides derived from monobasic acids** are obtained by distilling together an acid chloride with the sodium salt of the corresponding acid:

$$CH_3 . COCl + CH_3 . COONa \rightarrow \begin{matrix}CH_3 . CO \\ CH_3 . CO\end{matrix}\!\!>\!O + NaCl$$

Commercially they are obtained by the direct interaction of the sodium salt with half the quantity of phosphorus oxychloride or sulphuryl chloride required to form the acid chloride, whereby the acid chloride that is produced reacts with the excess of the sodium salt to yield the required anhydride. In the laboratory it is more satisfactory to isolate the chloride.

$$2CH_3 . COONa + SO_2Cl_2 \rightarrow 2CH_3 . COCl + Na_2SO_4$$
$$CH_3 . COCl + CH_3 . COONa \rightarrow NaCl + (CH_3 . CO)_2O$$

(see acetic anhydride, paragraphs **128, 129**).

Acid chlorides may be converted into the corresponding acid anhydrides by interaction with tertiary organic bases of the type of pyridine or quinoline in the presence of moisture. This method is only of importance for the preparation of aromatic anhydrides.

$$2C_6H_5 . COCl + H_2O + 2C_5H_5N \rightarrow (C_6H_5 . CO)_2O + 2C_5H_5N.HCl$$

PREPARATION 43. **ACETIC ANHYDRIDE,** $(CH_3.CO)_2O$

128. Reaction.—The mechanism of the reaction is described fully in the previous paragraph **127** (ii.).

129. Preparation.—Place 35 gm. of finely powdered, anhydrous sodium acetate, which has been recently dehydrated, in a tubulured retort, fitted with a dropping funnel and attached to a water condenser. By means of the dropping funnel add, drop by drop, 25 gm. of acetyl chloride. When the whole of the acetyl chloride has been added, remove the dropping funnel, replace it with a cork, and distil over the anhydride by means of a small luminous flame kept in constant motion. Purify the distillate by redistilling it, with the addition of 4 gm. of anhydrous sodium acetate, in an apparatus similar to that used for the purification of acetyl chloride (paragraph **52**). Collect the fraction between 135–140° C., and preserve it in a well-stoppered bottle. Yield, 25 gm.

Acetic Anhydride is a colourless liquid with a sharp, pungent odour. Insoluble in water, with which it slowly reacts; soluble in indifferent organic solvents. B.P. 137°; $\Delta = 1{\cdot}097$ (0° C.). For tests, see paragraph **284.**

ESTERS

130. Esterfication may be effected by—

(i.) *The interaction of an acid and an alcohol in the presence of a dehydrating agent,* such as strong sulphuric acid (see ethyl acetate, paragraphs **132, 133**).

(ii.) *The interaction of an acid and an alcohol in the presence of hydrochloric acid or other catalyst.*—This is known as the **Fischer synthesis** (see ethyl benzoate, paragraphs **134, 135**).

(iii.) *The interaction of the alcohol and an acid anhydride or acid chloride.*—Alcohols and phenols react readily with acid anhydrides and chlorides. With acid chlorides the reaction is greatly facilitated by the presence of alkalies (see phenyl benzoate, paragraphs **136, 137**).

(iv.) *The interaction of the alkyl sulphates and the alkali salts of the organic acids.*

$$CH_3 . COONa + C_2H_5O . SO_2 . ONa \rightarrow CH_3 . COOC_2H_5 + Na_2SO_4$$

Sodium ethyl sulphate

$$CH_3 . COONa + (CH_3)_2SO_4 \rightarrow CH_3 . COOCH_3 + CH_3O . SO_2 . ONa$$

Dimethyl sulphate

It should be noted that dimethyl sulphate is dangerously poisonous and should be handled only with the greatest care.

This reaction is analogous to the preparation of phenolic ethers by the agency of dimethyl sulphate (see methyl-β-naphthyl ether, paragraphs **147, 148**).

(v.) *The action of alkyl halides on the silver salts* of organic acids.

$$CH_3 . COOAg + C_2H_5I \rightarrow CH_3 . COOC_2H_5 + AgI$$

The two compounds are refluxed together for a short time, the silver halide filtered off, and the ester fractionated. Owing to the expensiveness of the reactants this method is only used when esterification by other methods is difficult.

(vi.) *The interaction of metallic sodium and an ester* results in the formation of an ester of the acetoacetic type with the elimination of a molecule of alcohol. (see acetoacetic ester, paragraphs **138, 139**). By the action of alkyl iodides on sodium acetoacetic ester, substituted acetoacetic esters are obtained,

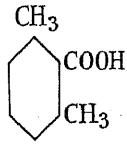
$$CH_3 . CO . \underset{\displaystyle Na}{\underset{|}{CH}} . COOC_2H_5 + C_2H_5I \rightarrow CH_3 . CO . \underset{\displaystyle C_2H_5}{\underset{|}{CH}} . COOC_2H_5 + NaI$$

Ethyl acetoacetic ester

from which important synthetic acids may be derived by acid hydrolysis (see paragraph **114** (viii.), and ethyl acetoacetic ester, paragraphs **140, 141**).

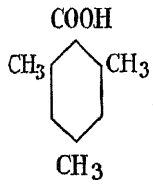
STERIC HINDRANCE

131. It is well known that di-ortho substituted acids, such as

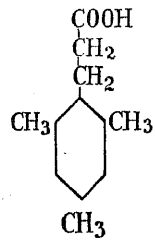


are hardly esterified at all, except by the silver salt method [paragraph **130** (v.)]. This is owing to a retardation of the rate of reaction, partly due to obstruction afforded by the surrounding groups, but mainly to the chemical influence exerted by the ortho-substituents. The extent of the interference varies with the nature of the groups present in the ortho-positions, and increases in the following order: chlorine, alkyl, phenolic, bromine, iodine, nitro.

Ortho-substituents do not retard esterification if the carboxyl group is remote from the nucleus, thus:



Is only slowly esterified



Is very easily esterified

PREPARATION 44. **ETHYL ACETATE,** $CH_3 . COOC_2H_5$.

132. Reaction.—The direct esterification of an alcohol by interaction with an organic acid is reversible:

$$CH_3 . COOH + C_2H_5OH \rightleftharpoons CH_3 . COOC_2H_5 + H_2O$$

and with equimolecular quantities of glacial acetic acid and absolute ethyl alcohol, equilibrium is established when about two-thirds of the alcohol has been esterified. The employment of a catalyst will shorten the time required to reach the equilibrium point, but will in no way alter the proportion of ester produced

finally, since a catalyst will accelerate both forward and reverse reactions to the same extent.

The most effective catalyst in esterification is the hydrogen ion, and therefore a freely ionised acid, such as hydrochloric acid, is used to promote the reaction. Sulphuric acid is much used when it has no chemical action on the organic acid used, since it not only acts as a catalyst, but also absorbs part of the water formed in the reaction, and thus prevents the reversibility of the reaction.

133. Preparation.—Fit a 500-c.c. distilling flask with a dropping funnel and attach to it a water condenser fitted with an adapter. In the flask place a mixture of 50 c.c. of concentrated sulphuric acid and 50 c.c. of absolute alcohol. Heat the flask in an oil bath to 140° C. and run in, by means of the dropping funnel, a mixture of 150 c.c. of glacial acetic acid and 150 c.c. of absolute alcohol. This mixture should be run in at the same rate as the ester distils over and collects in the receiver. When all the mixture of acid and alcohol has been added, stop the distillation, and wash the distillate in a beaker with sodium carbonate solution until the upper layer no longer reddens moistened blue litmus paper. Separate off the upper layer and shake it up with a solution of 50 gm. of calcium chloride in 50 c.c. of water to remove any remaining alcohol. Separate off the upper layer and dry it by means of anhydrous calcium chloride, and finally redistil the ester, using a water bath. Collect the fraction that distils between 76–78° C. Yield, 170 gm.

Ethyl Acetate is a colourless, mobile liquid, with an agreeable fruity odour, somewhat soluble in water and miscible with alcohol, ether and acetic acid. B.P. = 77° C.; $\Delta = 0{\cdot}924$ (0°/4°). For tests, see paragraph **286**.

Preparation 45. **ETHYL BENZOATE,** $C_6H_5 . COOC_2H_5$.

134. Reaction.—One of the most satisfactory methods of esterification is the *Fischer synthesis*, in which the organic acid is refluxed with an excess of absolute alcohol in which has been dissolved 3–5 per cent. of anhydrous hydrochloric acid gas. The ester is obtained by distilling off the excess of alcohol.

135. Preparation.—Dissolve 20 gm. of benzoic acid in 80 c.c. of absolute alcohol contained in a small, round-bottomed flask, and pass a current of dry hydrochloric acid until an increase of weight of 3 gm. is obtained. Reflux the solution on a water bath, using a water condenser, for three hours, and then distil off the excess of alcohol. Wash the residual ester twice with dilute sodium

carbonate solution, and then once with water. Dehydrate the oil by the addition of anhydrous calcium chloride and then redistil through an air condenser. Collect the fraction that distils between 211–213° C. Yield, 20 gm.

Ethyl Benzoate is a colourless oil with a characteristic and pleasant odour. It is insoluble in water, but is miscible with alcohol and ether. B.P. 212° C.; $\Delta = 1{\cdot}066$ (0°). For tests, see paragraph **286.**

PREPARATION 46. **PHENYL BENZOATE,** $C_6H_5 . COOC_6H_5$.

136. Reaction.—Alcohols and phenols react readily with acid anhydrides and acid chlorides to form esters :

$$\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>\!O + C_2H_5OH \rightarrow CH_3 . COOC_2H_5 + CH_3 . COOH$$

In the case of the acid chloride the reaction is so facilitated by the presence of caustic soda or potash that the esters are formed even in the presence of water.

$$C_6H_5OH + C_6H_5 . COCl + NaOH \rightarrow C_6H_5 . COOC_6H_5 + NaCl + H_2O$$

This reaction, which is known as the *Schotten-Baumann Reaction*, is also applicable for the production of substituted amides from primary and secondary amines (see benzanilide, paragraphs **161** and **330**).

137. Preparation.—Dissolve 6 gm. of phenol in 90 c.c. of water contained in a beaker, then add 9 gm. of benzoyl chloride. Make the solution alkaline with a solution of caustic soda and heat gently over a wire gauze for fifteen minutes, with stirring and shaking. Cool the liquid by immersing the beaker in cold water, and scratch the sides of the beaker with a sharp glass rod until the separated oil solidifies. Filter off the solid by means of the suction pump, and wash, first with dilute caustic soda solution and then with water. Recrystallise the product from methylated spirit. Yield, 10 gm.

Phenyl Benzoate is a colourless solid, soluble in alcohol and ether. M.P. = 68–69°; B.P. = 314°. For tests, see paragraph **285.**

PREPARATION 47. **ACETOACETIC ESTER,** $CH_3 . CO . CH_2 . COOC_2H_5$.

138. Reaction.—It was discovered by *Geuther* in 1863 that by the action of sodium on ethyl acetate an ester, acetoacetic ester, was formed by condensation. The mechanism of the reaction was subsequently explained by *Claisen.*

The sodium added first reacts with the alcohol, which must be present in small quantity, and the resultant sodium ethylate reacts additively with a molecule of the ester :

$$CH_3 . COOC_2H_5 + C_2H_5ONa \rightarrow CH_3 . C\begin{cases} OC_2H_5 \\ -OC_2H_5 \\ ONa \end{cases}$$

This compound reacts with a further molecule of the ester, producing sodium ethyl acetoacetate.

$$CH_3 . C\begin{cases} OC_2H_5 \\ -OC_2H_5 \\ ONa \end{cases} + \begin{matrix} H \\ \\ H \end{matrix}\!\!>\!CH . COOC_2H_5 \rightarrow CH_3 . \underset{\underset{ONa}{|}}{C} : CH . COOC_2H_5 + 2C_2H_5OH$$

The sodium compound is then decomposed with acetic acid, yielding the free ester, which, however, is tautomeric, and at the ordinary temperature consists almost entirely of the ketonic form :

$$\underset{\text{Enolic form}}{CH_3 . \underset{\underset{OH}{|}}{C} = CH . COOC_2H_5} \rightleftharpoons \underset{\text{Ketonic form}}{CH_3 . \underset{\underset{O}{\|}}{C}-CH_2 . COOC_2H_5}$$

The great importance of the esters of this type lies in the reactivity of their sodium compounds towards organic halogen compounds, and the fact that the resultant substituted acetoacetic esters may undergo saponification in two ways, namely, (1) ketonic hydrolysis, and (2) acid hydrolysis, thus—

$$(1)\quad H_2O + CH_3 . CO . C . R_1R_2- \mid COOC_2H_5 \xrightarrow[\text{or } Ba(OH)_2]{\text{Dilute NaOH}} CH_3 . CO . CHR_1R_2 + CO_2 + C_2H_5OH$$

$$(2)\quad 2H_2O + CH_3 . CO . \mid C . R_1 . R_2 . COOC_2H_5 \xrightarrow[\text{or HCl}]{\text{Conc. NaOH}} CH_3 . COOH + HC . R_1R_2 . COOH + C_2H_5OH$$

It should be noted, however, that it is almost impossible to bring about the one type of hydrolysis to the complete exclusion of the other (see paragraphs **140**, **114** (viii.), and **88** (vi.)).

139. Preparation.—*Note.*—The preparation of acetoacetic ester should be commenced in the morning, so that the whole experiment may be completed in the one day.

Place 20 gm. of sodium, cut into very thin slices, in a dry round-bottomed flask, of 1 litre capacity, to which is fitted an efficient reflux water condenser. Pour down through the inner tube of the condenser 200 gm. of *anhydrous* ethyl acetate (paragraphs **132**, **133**). When the reaction has slackened, which will take about

fifteen minutes, reflux gently on a previously heated water bath until all the sodium has dissolved. This operation will take from three to four hours. Acidify the warm liquid with glacial acetic acid diluted with its own volume of water. About 130 c.c. of the diluted acid will be required. Add 300 c.c. of a cold, saturated solution of common salt and shake. Separate off the upper layer, which is a mixture of acetic and acetoacetic esters. To separate these two esters distil through a water condenser over a naked, luminous flame until the thermometer immersed in the vapour reaches 95° C. The distillate contains the unchanged ethyl acetate. Fractionate the residue in the distillation flask under reduced pressure, as described in paragraph **11**. Small quantities of water, acetic acid and ethyl acetate distil over first and then the acetoacetic ester, which boils at

75° C. at 15 mm. pressure,
80° C. at 19 mm. pressure.
95° C. at 50 mm. pressure.

Yield, 48 gm.

Acetoacetic Ester is a colourless liquid with a pleasant odour, soluble in alcohol and ether. B.P. = 180·5°, with decomposition. $\Delta = 1{\cdot}046$ (0°/4°). For tests, see paragraph **286**.

PREPARATION 48. ETHYL ACETOACETIC ESTER, $CH_3 . CO . CH(C_2H_5) . COOC_2H_5$

140. Reaction.—The sodium derivatives of the acetoacetic compounds react readily with organic halogen compounds, yielding substituted acetoacetic esters:

$$CH_3 - C(ONa) = CH . COOC_2H_5 + C_2H_5I \rightarrow NaI + \underset{\text{Ethyl acetoacetic ester}}{CH_3 . CO . CH(C_2H_5) . COOC_2H_5}$$

The second hydrogen atom may then be replaced with sodium and allowed to interact with an alkyl halide in precisely the same way:

$$CH_3 - C(ONa) = C(C_2H_5) - COOC_2H_5 + C_2H_5 \rightarrow CH_3 . CO . C(C_2H_5)_2 . COOC_2H_5 + NaI$$

Diethyl acetoacetic ester

The sodium compounds not only react with alkyl halides, but also with acid chlorides, and with halogen substituted acids. Thus, sodium acetoacetic ester and benzoyl chloride give benzoyl acetoacetic ester :

$$CH_3 . CO . CH(CO . C_6H_5) . COOC_2H_5$$

and chloracetic ester gives acetylsuccinic ester :

$$CH_3 . CO . CH(CH_2 . COOC_2H_5) . COOC_2H_5$$

The compounds derived from these substituted esters on saponification are described in paragraph **138.**

141. Preparation.—Add cautiously 6 gm. of sodium to 100 c.c. of absolute alcohol contained in a round-bottomed flask fitted with a reflux water condenser. When all the sodium has dissolved, cool the flask by immersion in crushed ice and add 33 gm. of acetoacetic ester. Now add, drop by drop, 40 gm. of ethyl iodide. When all the iodide has been added, warm the mixture on the water bath until neutral to moist litmus paper. If necessary add a little more ethyl iodide to render the liquid neutral. Distil off the alcohol, heating the flask over a water bath, shake the residue remaining in the flask with water until all the solid matter dissolves, and then extract the aqueous solution with ether. Separate and dehydrate the ethereal solution with anhydrous calcium chloride and distil off the ether. Fractionate the residue under reduced pressure and collect the distillate with a B.P. of 84° at 15 mm. pressure or with a B.P. of 91° at 20 mm. pressure. Yield, 30 gm.

Diethyl Acetoacetic Ester ($CH_3CO . C(C_2H_5)_2 . COOC_2H_5$) may be prepared from the mono-ethyl derivative by treatment with sodium and then ethyl iodide, as in the above preparation. The diethyl derivative boils at 93° at 15 mm. pressure, and a yield of about 60 per cent. is obtained.

Ethyl Acetoacetic Ester is a colourless liquid, boiling with slight decomposition at 198°. $\Delta = 0{\cdot}998$ (12°). For tests, see paragraph **286.**

Diethyl Acetoacetic Ester is a colourless liquid, boiling with slight decomposition at 218°. $\Delta = 0{\cdot}974$ (20°).

ETHERS

142. The aliphatic ethers are produced by the action of concentrated sulphuric acid on the alcohols, particularly in the presence of anhydrous aluminium sulphate, which acts catalytically (see ether, paragraphs **143, 144**).

The ethers containing two different radicals are best obtained by the interaction of the alcoholates and the alkyl halides (*Williamson's synthesis*):

$$C_2H_5ONa + CH_3I \rightarrow C_2H_5 . O . CH_3 + NaI$$

and the phenolic ethers similarly by the action of halides on the anhydrous phenates (see benzyl-*p*-nitrophenol ether, paragraphs **145, 146**).

Phenolic methyl ethers are easily obtained by the action of dimethylsulphate on aqueous solutions of the phenates containing excess of alkali (see β-naphthyl methyl ether, paragraphs **147, 148**).

Commercially some aromatic ethers are obtained catalytically by the action of thoria on the vapour of the phenol or naphthol at a temperature of from 300–400° C. Mixed ethers, such as the methyl naphthyl ethers, are also obtained in this way:

$$CH_3OH + C_{10}H_7OH \xrightarrow[ThO_2]{300^\circ} CH_3 . O . C_{10}H_7 + H_2O$$

PREPARATION 49. **DIETHYL ETHER,** $C_2H_5 . O . C_2H_5$.

143. Reaction.—The formation of an ether from an alcohol by treatment with sulphuric acid is preceded by the production of an alkyl sulphuric acid:

$$C_2H_5OH + H_2SO_4 \xrightarrow[140^\circ]{} C_2H_5 . HSO_4 + H_2O$$

$$C_2H_5 . HSO_4 + C_2H_5OH \rightarrow C_2H_5 . O . C_2H_5 + H_2SO_4$$

In practice, therefore, alcohol is added continuously to the hot reaction mixture at the same rate as the ether distils off. At higher temperatures the alkyl sulphuric acids decompose to produce ethylenes.

Anhydrous aluminium sulphate greatly facilitates the reaction, which then takes place at a much lower temperature.

144. Preparation.—Fit a distilling flask with a thermometer and

a tap funnel, both reaching almost to the bottom of the flask. Attach the flask to a long and efficient water condenser, leading, by way of an adapter, into a receiver immersed in a mixture of ice and salt. Add slowly, with cooling, 100 gm. of concentrated sulphuric acid to an equal weight of industrial alcohol. Next add 20 gm. of anhydrous aluminium sulphate and place the mixture in the distilling flask. The thermometer and the tap funnel must both dip *into* the acid mixture. Heat the whole on a sand bath until the temperature reaches 110° C., when the ether commences to distil over. Maintain the temperature at 110–120°, and run in about 100 c.c. of alcohol at the same rate as the ether distils over. Wash the distillate twice with 50 c.c. of dilute caustic soda solution and then once with a saturated solution of salt. Dry the ether with anhydrous calcium chloride and redistil from a water bath with great care, since it is highly inflammable. Yield, 100 gm.

Diethyl Ether is a colourless liquid with an ethereal odour. It is soluble in 12 parts of water and is miscible with alcohol. B.P. 35° C.; $\Delta = 0{\cdot}719$ (15°/4°). For tests, see paragraph **298.**

PREPARATION 50. BENZYL *p*-NITROPHENYL ETHER, $C_6H_5 . CH_2 . O . C_6H_4 . NO_2$.

145. Reaction.—Phenolic ethers are conveniently obtained by the interaction of halides, such as the alkyl halides, benzyl chloride or picryl chloride, with the anhydrous sodium phenates. The reaction is usually quantitative. The reactants are refluxed together in the presence of anhydrous chloroform, containing a trace of absolute alcohol, or in absolute alcohol alone.

$$C_6H_5 . CH_2Cl + NaO . C_6H_4 . NO_2 \rightarrow NaCl + C_6H_5CH_2 . O . C_6H_4 . NO_2$$

By the use of acid chlorides in chloroform solution, phenolic esters are readily obtained in quantitative yield:

$$C_6H_5 . COCl + NaO . C_6H_5 \rightarrow \underset{\text{Phenyl benzoate}}{C_6H_5 . COOC_6H_5} + NaCl$$

146. Preparation.—Dissolve 20 gm. of para-nitrophenol in a warm solution of 6 gm. of sodium hydroxide in about 100 c.c. of water, contained in a porcelain dish. Evaporate the solution to a small bulk, add an equal volume of absolute alcohol, and allow to cool, when the sodium salt of the nitrophenol will crystallise out. Filter off the crystallised salt, which is bright yellow in colour, and wash it with a few cubic centimetres of absolute alcohol. Dry the salt for two hours in an air oven at 110° C., and then allow it to cool in a vacuum desiccator containing strong sulphuric acid.

Reflux together for one hour, over a water bath, 15 gm. of the anhydrous sodium nitrophenol, 15 gm. of benzyl chloride, and 150 c.c. of absolute alcohol. Filter the hot solution through a previously warmed Buchner funnel, when the bulk of the benzyl ether will crystallise out on cooling in pure white crystals. Filter off the crystals and wash them first with alcohol and then with water, and dry. The remainder of the compound may be recovered from the mother-liquor by steam distillation, which removes the excess of benzyl chloride and the bulk of the alcohol. The yield is quantitative.

Benzyl *p*-Nitrophenyl Ether crystallises in fine white needles, only very slightly soluble in alcohol, ether and glacial acetic acid. The compound is very stable and is not decomposed by alcoholic potash. M.P. 105·4°.

PREPARATION 51. METHYL β-NAPHTHYL ETHER, $CH_3 . O . C_{10}H_7$.

147. Reaction.—The methyl ethers of the phenols are conveniently obtained by the action of dimethyl sulphate on the phenol dissolved in an excess of sodium hydroxide solution. A slight excess of dimethyl sulphate is also used.

$$C_{10}H_7 . ONa + (CH_3)_2SO_4 \rightarrow C_{10}H_7 . O . CH_3 + Na . CH_3 . SO_4$$

Caution.—**Dimethyl sulphate is very poisonous, and although it boils at 188°, the vapour evolved at the normal temperature has been known to cause death. It is readily absorbed through the skin, and precautions must be taken not to spill any on the hands or clothes.**

148. Preparation.—Dissolve 14·4 gm. of β-naphthol in 50 c.c. of water, containing 5 gm. of caustic soda. Add 12 c.c. of dimethyl sulphate and warm the liquid gently, with shaking. After thirty minutes, standing, reflux for fifteen minutes on a water bath to destroy the excess of dimethyl sulphate, more caustic soda solution being added, if necessary, to maintain an alkaline reaction. Add an equal volume of water and filter off the precipitated naphthyl ether. Wash with water and recrystallise from methylated spirits. Yield, 15 gm.

Methyl β-Naphthyl Ether crystallises in lustrous plates with an odour like oil of neroli (orange-blossom). Soluble with some difficulty in alcohol, but easily in ether. M.P. 72°; B.P. 274°. For tests, see paragraph **297**.

AMIDES AND SUBSTITUTED AMIDES

149. Acid Amides are prepared by the following general methods:

(i.) *The distillation of the ammonium salts* of the corresponding fatty acids:

$$CH_3 . COONH_4 \rightarrow CH_3 . CONH_2 + H_2O$$

(see acetamide, paragraphs **151, 152**).

(ii.) *The interaction of ammonia and acid chlorides, acid anhydrides or esters:*

$$CH_3 . COCl + 2NH_3 \rightarrow CH_3 . CONH_2 + NH_4Cl$$

$$\begin{matrix} CH_3 . CO \\ \\ CH_3 . CO \end{matrix} \!\!>\!\! O + 2NH_3 \rightarrow CH_3 . CONH_2 + CH_3 . COONH_4$$

$$CH_3 . COOC_2H_5 + NH_3 \rightarrow CH_3 . CONH_2 + C_2H_5OH$$

(see oxamide, paragraphs **153, 154**).

(iii.) *The hydrolysis of nitriles*, in the cold, with hydrogen peroxide in the presence of caustic soda:

$$2CH \vdots CN + 2H_2O_2 \rightarrow 2CH_3 . CONH_2 + O_2$$

(see benzamide, paragraphs **155, 156**).

150. Substituted Amides are produced by the following general methods:

(i.) *The interaction of primary amines with acids* on heating:

$$CH_3 . COOH + C_6H_5 . NH_2 \rightarrow C_6H_5 . NH . COCH_3 + H_2O$$

(see *p*-nitroformanilide, paragraphs **157, 158**).

(ii.) *The interaction of primary or secondary amines and acid anhydrides*, with or without a condensing agent, such as strong sulphuric acid:

$$\begin{matrix} CH_3 . CO \\ \\ CH_3 . CO \end{matrix} \!\!>\!\! O + C_6H_5 . NH_2 \rightarrow CH_3 . COOH + C_6H_5 . NH . COCH_3$$

(see acetanilide, paragraphs **159, 160**).

(iii.) *The interaction of acid chlorides and primary amines*, either alone, or in an inert solvent; or in the case of the stable aromatic chlorides, in the presence of caustic soda, by the *Schotten-Baumann Reaction*, paragraph **136**.

$$C_6H_5 . NH_2 + C_6H_5 . COCl + NaOH \rightarrow C_6H_5 . NH . COC_6H_5 + NaCl + H_2O$$

(see benzanilide, paragraphs **161, 162**, also paragraph **330**).

For the preparation of thioamides and thioanilides, see paragraph **165.**

PREPARATION 52. **ACETAMIDE,** $CH_3 . CONH_2$.

151. Reaction.—The preparation of an acid amide by the distillation of an ammonium salt is a general method of obtaining these compounds. Better yields are obtained if the salt is heated in a sealed tube for five or six hours to about 220° C., and the product purified by subsequent distillation.

$$CH_3 . COONH_4 \rightarrow CH_3 . CONH_2 + H_2O$$

152. Preparation.—Melt 50 gm. of ammonium acetate and pour into a bomb tube (**406**) previously warmed in a luminous flame. Clean the open end of the bomb tube from adhering material by melting down with a flame, and wipe with a cloth or filter paper. Seal off the tube as described in paragraph **406.** Heat the tube in a bomb furnace (**406**) at 210–220° for six hours. Open the tube when cold, and transfer the liquid reaction-product to a flask fitted with a thermometer and attached to an air condenser. Heat the flask with a naked flame and distil; at first water and acetic acid will pass over. When the temperature reaches 180° C. change the receiver and collect in a beaker all that passes over below 230° C. Cool this fraction in powdered ice and salt, scratching the sides of the beaker meanwhile with a glass rod. Free the solid amide thus obtained from adherent mother-liquor by pressing it between filter paper, or by placing it on a porous plate. Redistil the crystals, collecting the fraction between 210–225° C. The distillate, which smells strongly of mice, due to the presence of a small quantity of an impurity, may be purified by recrystallisation from benzene or chloroform, when almost odourless, colourless crystals of acetamide are obtained. Yield, 20 gm.

Acetamide crystallises in clear needles. Very soluble in cold water and alcohol, but with difficulty in ether. M.P. = 82–83°; B.P. 222°. For tests, see paragraph **326.**

PREPARATION 53. **OXAMIDE,** $\begin{matrix} CO—NH_2 \\ | \\ CO—NH_2 \end{matrix}$

153. Reaction.—Acid amides are readily obtained by the action of concentrated ammonia on esters. In practice the ester is added gradually to a large excess of strong ammonia solution:

$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + 2NH_3 \rightarrow \begin{matrix} CO . NH_2 \\ | \\ CO . NH_2 \end{matrix} + 2C_2H_5OH$$

154. Preparation.—Place 100 c.c. of concentrated ammonia solution ($\Delta = 0{\cdot}880$), in a round-bottomed flask, and add slowly, with shaking, 10 gm. of diethyl oxalate. Leave for half an hour, and dilute with 150 c.c. of water. Filter off the white crystalline precipitate on a Buchner funnel, wash well with water and dry on a porous plate. Yield, 4 gm.

Oxamide is a colourless, odourless, crystalline powder. Insoluble in water, alcohol and ether. Melts at 415°, with decomposition, if heated in a sealed tube. On heating in an open tube it sublimes with partial decomposition. For tests, see paragraph **326**.

PREPARATION 54. **BENZAMIDE,** $C_6H_5 . CO . NH_2$.

155. Reaction.—In the saponification of nitriles the acid amide is first produced, but the amide is not usually readily isolated, since it undergoes further hydrolysis :

$$R . C \vdots N \xrightarrow{H_2O} R . CO . NH_2 \xrightarrow{H_2O} R . COOH + NH_3$$

By the action of hydrogen peroxide in the presence of caustic soda in the cold, the reaction does not proceed beyond the first stage, and the amide is obtained in quantitative yield.

$$2R . C \vdots N + 2H_2O_2 \rightarrow 2R . CO . NH_2 + O_2$$

156. Preparation.—Add 10 gm. of benzonitrile to about 150 c.c. of ten-volume hydrogen peroxide solution previously mixed with 5 c.c. of 2N sodium hydroxide. Warm the whole in an open flask on a water bath to 40° and then shake vigorously until all the oil has disappeared, and only a white precipitate is present. Owing to the evolution of oxygen which takes place, the flask must not be corked.

Filter off the precipitated benzamide, wash with water, and recrystallise from very dilute methylated spirit. Yield, 10 gm.

Benzamide crystallises in odourless, monoclinic tablets from water. The compound is only slightly soluble in water, but is easily soluble in alcohol, ether and hot benzene. M.P. 126°. For tests, see paragraph **326**.

PREPARATION 55. *p*-**NITROFORMANILIDE,** $NO_2 . C_6H_4 . NH . OCH$.

157. Reaction.—Formanilides and acetanilides may be prepared by refluxing together for some hours a mixture of the primary amine and the pure acid. Formic acid, which is a much stronger acid than acetic, reacts readily :

$$NO_2 . C_6H_4 . NH_2 + H . COOH \rightarrow NO_2 . C_6H_4 . NH . OCH + H_2O$$

158. Preparation.—Place a mixture of 20 gm. of para-nitraniline and 30 c.c. of anhydrous formic acid in a small round-bottomed flask. Reflux this mixture for four hours on a water bath. Now add 100 c.c. of water, shake, allow to cool, and filter off the solid product. Recrystallise the compound from dilute methylated spirit. Yield, 18 gm.

The ortho- and meta-isomerides may be prepared in a precisely similar manner.

p-**Nitroformanilide** crystallises in golden brown needles, soluble in alcohol, and somewhat soluble in hot water. M.P. = 192°.

o-**Nitroformanilide** crystallises in large, golden needles, soluble in alcohol, and moderately soluble in hot water. M.P. = 122°.

m-**Nitroformanilide** crystallises in yellow needles, soluble in alcohol and in hot water, but difficultly soluble in ether and ligroin. M.P. = 134°.

PREPARATION 56. **ACETANILIDE,** $C_6H_5 . NH . CO . CH_3$.

159. Reaction.—Primary and secondary amines may be converted unto their acyl derivatives by the action of acid anhydrides. The derivatives of the secondary amines, and the di-acyl compounds of the primary amines, are only prepared with great difficulty :

$$C_6H_5 . NH_2 + \begin{matrix} CH_3 . CO \\ CH_3 . CO \end{matrix} \!\!>\!\! O \rightarrow C_6H_5 . NH . CO . CH_3 + CH_3 . COOH$$

If acetylation does not proceed easily the addition of 1 or 2 drops of strong sulphuric acid usually causes the reaction to proceed immediately and quickly.

160. Preparation.—Add slowly 10 gm. of aniline to 12 gm. of acetic anhydride contained in a small round-bottomed flask. When the vigorous reaction has slackened, warm the flask on a water bath for fifteen minutes, and then pour the contents into boiling water containing a little hydrochloric acid. Filter off the precipitated acetanilide when cold, and recrystallise from dilute methylated spirit. Yield, 14 gm.

Acetanilide crystallises in odourless, colourless leaflets from hot water. It is soluble in 18 parts of boiling water, and very soluble in hot alcohol, ether and chloroform. M.P. = 114·2°; B.P. = 304°. For tests, see paragraph **331.**

PREPARATION 57. **BENZANILIDE,** $C_6H_5 . NH . COC_6H_5$.

161. Reaction.—Substituted amides are readily produced from the more stable aromatic acid chlorides by the **Schotten-Baumann**

Reaction, the primary amine being suspended in dilute sodium hydroxide solution and an excess of the chloride added little by little with continuous shaking.

$$C_6H_5NH_2 + C_6H_5 . COCl + NaOH \rightarrow C_6H_5 . NH . COC_6H_5 + H_2O + NaCl$$

For the preparation of phenolic esters by this reaction, see paragraph **136,** and also see paragraph **330.**

162. Preparation.—Shake up 10 gm. of aniline with about 150 c.c. of 10 per cent. caustic soda solution, and add 18 gm. of benzoyl chloride in five portions, shaking vigorously after each addition until the smell of benzoyl chloride disappears. The solution should not be allowed to get warm. When all the benzoyl chloride has been added, filter off the solid benzanilide, and wash on the filter successively with cold caustic soda solution, with water, with dilute hydrochloric acid, and finally with water. Recrystallise from dilute methylated spirit. Yield, 18 gm.

Benzanilide crystallises in odourless leaflets from alcohol. It is insoluble in water, but easily soluble in alcohol and ether. M.P. 160°. Distils without decomposition. For tests, see paragraph **331.**

PREPARATION 58. **UREA (CARBAMIDE),** $O = C\begin{matrix}NH_2\\NH_2\end{matrix}$

163. Reaction.—Urea, the di-amide of carbonic acid, can be obtained by the general reactions already discussed in this section, such as :

(i.) The interaction of ammonia and the acid chloride :

$$COCl_2 + 4NH_3 \rightarrow OC(NH_2)_2 + 2NH_4Cl$$

(ii.) The interaction of ammonia and a carbonic ester :

$$OC . (OC_2H_5)_2 + 2NH_3 \rightarrow OC . (NH_2)_2 + 2C_2H_5OH$$

(iii.) The action of heat on ammonium carbonate, the aqueous solution being heated under pressure :

$$OC . (ONH_4)_2 \rightarrow OC . (NH_2)_2 + 2H_2O$$

It is often prepared by the **Wöhler synthesis,** *i.e.*, by the molecular rearrangement of ammonium cyanate on heating :

$$NH_4CNO \rightarrow OC : (NH_2)_2$$

This was the first organic compound to be prepared by artificial means, and by its synthesis in 1828 Wöhler laid the foundations of synthetic organic chemistry.

164. Preparation.—Heat 50 gm. of pure potassium cyanide in

an iron dish, under a hood, until it begins to fuse, and then stir in 150 gm. of red lead:

$$4KCN + Pb_3O_4 \rightarrow 4KCNO + 3Pb$$

When the reaction has subsided pour the dark liquid on to an iron plate, and when cold separate the mass from the metallic lead. Powder the crude cyanate and extract with about 200 c.c. of cold water; allow to stand for an hour and filter. Add a saturated solution of 25 gm. of ammonium sulphate to the filtrate and evaporate to dryness on a water bath with stirring. Powder the residue when cold, and extract the urea from it with four successive 50 c.c. of hot absolute alcohol. From the combined alcoholic extracts distil off the greater part of the alcohol from a water bath; then pour out the residual liquid to crystallise. Yield, 12 gm.

Urea crystallises in 4-sided prisms from water, but in needles if very rapidly crystallised. It is very soluble in cold water, soluble in 20 parts cold alcohol, and almost insoluble in chloroform. M.P. 132°. For tests, see paragraph **326**.

PREPARATION 59. **THIOCARBANILIDE,** $S : C\begin{<}NH \cdot C_6H_5 \\ NH \cdot C_6H_5$

165. Reaction.—Thioamides and thioanilides are obtained by heating together the corresponding amides or anilides with phosphorus pentasulphide. In the case of the amides a large volume of an inert solvent is used so as to prevent dehydration of the amide to the nitrile:

$$5C_6H_5 \cdot CO \cdot NH_2 + P_2S_5 \rightarrow 5C_6H_5 \cdot CS \cdot NH_2 + P_2O_5$$

Thioamides are also obtained by the direct addition of sulphuretted hydrogen to the nitrile in alcoholic solution containing ammonia:

$$CH_3 \cdot CN + H_2S \rightarrow CH_3 \cdot CS \cdot NH_2$$

The di-aryl thioureas are, however, most conveniently obtained by the interaction of the primary amine and carbon disulphide, in the presence of sulphur as a catalyst:

$$2C_6H_5NH_2 + CS_2 \rightarrow S : C\begin{<}NH \cdot C_6H_5 \\ NH \cdot C_6H_5 + H_2S$$

166. Preparation.—Reflux together on the water bath a mixture of 20 gm. of aniline, 20 gm. of carbon disulphide, 20 gm. of absolute alcohol, and 0·25 gm. of sulphur. The flask used must be provided with an efficient water condenser, and the operation, which will occupy six hours, should be carried out in a fume chamber.

Next distil off the excess of carbon disulphide and alcohol, and wash the residue first with water, then with dilute hydrochloric acid, and lastly again with water. Recrystallise from dilute methylated spirit. Yield, 20 gm.

Thiocarbanilide crystallises in colourless, rhombic prisms. It is soluble in alcohol and ether, but almost insoluble in water. M.P. 153°. For tests, see paragraph **354.**

NITROSO-COMPOUNDS

167. The nitroso-compounds of phenols and tertiary amines of the aromatic series are readily prepared by the direct action of nitrous acid in the cold, the nitroso-group invariably entering the para-position to the phenolic or amino-group:

$$C_6H_5OH + HONO \rightarrow HO \cdot C_6H_4 \cdot NO + H_2O$$

see *p*-nitrosophenol (paragraph **168**) and *p*-nitrosodimethylaniline (paragraph **170**).

The other nitroso-compounds are of little importance. They can be prepared by the oxidation of amines with permonosulphuric acid, or from the aromatic hydroxylamines by oxidation with chromic acid or ferric chloride:

$$C_6H_5NH_2 + O \xrightarrow{H_2SO_5} C_6H_5 \cdot NO + H_2O$$

$$C_6H_5 \cdot NHOH + O \xrightarrow{H_2CrO_4} C_6H_5 \cdot NO + H_2O$$

Solid nitroso-hydrocarbons are in the bimolecular state; they are colourless and crystalline, but when fused or in solution, they become monomolecular and are emerald green in colour. They have a piercing odour and are very volatile.

The *p*-nitrosophenols are identical with the quinone monoximes (paragraph **100**), and the *iso*-nitroso compounds correspond to the monoximes of the *a*-diketones (see camphor quinone monoxime, paragraphs **106**, **107**).

PREPARATION 60. *p*-NITROSOPHENOL, $HO \cdot C_6H_4 \cdot NO$.

168. Reaction.—Aromatic phenols readily react with nitrous acid to form para-nitroso compounds. These compounds are identical with the quinone monoximes, as shown in paragraph **100.**

The para-nitrosophenols are also obtained by the hydrolysis of the para-nitroso-tertiary amines with boiling solutions of alkali:

$$ON \cdot C_6H_4 \cdot N(CH_3)_2 + KOH \rightarrow ON \cdot C_6H_4 \cdot OK + HN \cdot (CH_3)_2$$

(see diethylamine, paragraph **186**).

169. Preparation.—Dissolve 10 gm. of phenol and 35 gm. of potassium nitrite in 1,500 c.c. of cold water. Add powdered ice and then add slowly, with continual stirring, 25 c.c. of glacial acetic acid, previously diluted to 300 c.c. with ice-water. Leave

the mixture for twelve hours and then extract with ether. Shake the ethereal extract with an equal volume of a *concentrated* solution of caustic soda, when brown crystals of the sodium nitrosophenate separate. Filter off the crystals through a Buchner funnel and press them on a porous plate to free them from adherent liquor. Redissolve the crystals in a little water and acidify with dilute sulphuric acid. When cold, filter off the precipitated nitrosophenol, and dissolve and recrystallise from a mixture of benzene and acetone. Yield, 11 gm.

p-**Nitrosophenol** crystallises in yellowish green needles. It is moderately soluble in water, but readily soluble in alcohol, acetone, ether and alkalies. It dissolves with some difficulty in glacial acetic acid and liquid hydrocarbons. It melts, with decomposition, from 120–130°. For tests, see paragraph **319**.

PREPARATION 61. *p*-NITROSODIMETHYLANILINE, $ON . C_6H_4 . N(CH_3)_2$.

170. Reaction.—Nitrous acid reacts directly with aromatic tertiary amines of the type of dimethylaniline, the nitroso-group entering the nucleus in the para-position to the amino-group.

With boiling solutions of alkalies these nitroso-compounds are split up into nitrosophenols and secondary aliphatic amines (paragraphs **168, 186**).

171. Preparation.—Dissolve 20 gm. of dimethylaniline, contained in a beaker, in a mixture of 50 c.c. of concentrated hydrochloric acid and 100 c.c. of water. Cool by immersing the beaker in a mixture of powdered ice and salt. Dissolve 12 gm. of sodium nitrite in 20 c.c. of water and cool, and then add, in very small quantities, this solution to that of the amine, stirring continuously. Allow to stand for one hour. Filter off the crystalline hydrochloride of nitrosodimethylaniline and wash with 50 c.c. of methylated spirit containing 3 c.c. of strong hydrochloric acid. Recrystallise from a minimum quantity of boiling water. Yield, 28 gm.

Dissolve 12 gm. of the above hydrochloride in water, and add cold caustic soda solution till alkaline, and extract the free base with ether. Dehydrate the ethereal solution with anhydrous calcium chloride. Distil off the bulk of the ether, and set aside the remainder to cool. The *p*-nitrosodimethylaniline separates in brilliant green crystals. Yield, 9 gm.

p-**Nitrosodimethylaniline** crystallises in bright green scales. It dissolves with difficulty in water, giving a dark brown solution ;

but is readily soluble in alcohol and ether. M.P. 85°. For tests, see paragraph **319**.

p-**Nitrosodimethylaniline Hydrochloride** crystallises in bright orange-yellow needles. It is soluble in water, but insoluble in organic solvents.

NITRO-COMPOUNDS

172. The aromatic nitro-compounds are always prepared by direct nitration. The position of the entering nitro-group, and the ease with which nitration is effected, are both dependent on the groups already present in the nucleus. The effect of other groups may be shown thus :

$$\underset{\text{The above groups exert a retarding influence and yield the meta-isomeride principally.}}{\longleftarrow\ -NO_2\ \ -SO_3H\ \ -CHO\ \ -COOH\ \ -Cl\ \longrightarrow}\ \underset{\text{The above groups exert an accelerating influence and yield a mixture of the ortho- and para-isomerides.}}{-CH_3\ \ -NH_2\ \ -OCH_3\ \ -OH}$$

In all nitrations the temperature must be kept under rigid control, or else the reaction is liable to proceed violently and get

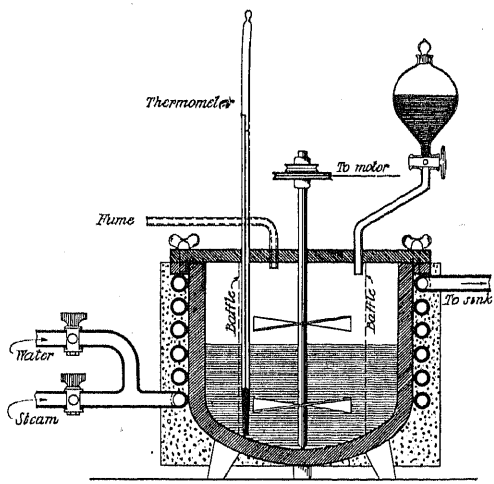


FIG. 25.—Nitrator.

out of hand. The temperature of nitration, and the concentration of nitric acid used, have practically no influence on the relative amount of each isomeride produced. The control of temperature is much more easily maintained by the use of a small nitrator, such as that shown in Fig. 25. The nitrator should be made of cast iron for use with strong mixtures of nitric and sulphuric acids, and of aluminium for use with dilute nitric acid alone.

Amines and phenols on nitration tend to give large quantities of resinous and tarry products, and hence amino- and phenolic

groups are protected by acetylation before nitration. The phenols can be directly nitrated in organic solvents, such as glacial acetic acid, see nitrophenol (paragraph **177**) and nitraniline (paragraph **179**).

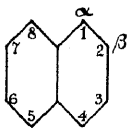
For the nitration of the hydrocarbons and their derivatives, which are not easily nitrated, nitric acid admixed with a considerable amount of strong sulphuric acid is used. This mixture is known always as *mixed acid*. The sulphuric acid accelerates the reaction, absorbing the water formed :

$$C_6H_6 + HNO_3 \rightarrow C_6H_5 . NO_2 + H_2O$$

Solvents in which nitric acid is soluble, such as glacial acetic acid and acetic anhydride, may be used with advantage for the nitration of phenols and other compounds. The formation of tarry substances is thereby considerably diminished, since all the components of the reaction are in homogeneous solution, and hence nitration proceeds regularly, whereas in aqueous solution the acid mixture can react only with the exposed surfaces of the oily globules. The nature of the solvent used has a directive influence on the reaction in the case of anilides and related substances. Thus, whereas acetanilide in acetic anhydride solution, gives a large amount of the ortho-nitro-derivative, in strong sulphuric acid solution, the para-compound is formed almost exclusively (paragraph **179**).

Mercury and the mercuric salts tend to promote catalytic oxidation, followed by subsequent nitration. Thus benzene and the alkyl benzenes react with dilute nitric acid, in the presence of mercury, to give nitrophenols.

Naphthalene and its derivatives yield on nitration α-nitro-compounds, dinitration giving a mixture of the 1 : 5 and 1 : 8 derivatives :



It is not possible to nitrate into the β-position, and therefore the β-compounds have to be prepared from the β-sulphonic acid and its derivatives (see β-naphthylamine (paragraph **196**)).

PREPARATION 62. **NITROBENZENE,** $C_6H_5 . NO_2$.

173. Reaction.—The nitration of a hydrocarbon is effected with "mixed acid," *i.e.*, an acid containing about 2 parts of strong

sulphuric acid to 1 part of nitric acid ($\Delta = 1{\cdot}42$). The acid mixture is added in instalments to the benzene, with continuous shaking.

The resultant nitro-compounds are usually yellow in colour, and have a much higher boiling-point and specific gravity than the parent substances. They are not, as a rule, very soluble in water, but often appreciably soluble in strong sulphuric acid.

174. Preparation.—Carefully pour 50 c.c. of strong sulphuric acid into 50 c.c. of pure nitric acid, $\Delta = 1{\cdot}42$, and cool. Slowly add the acid mixture, in small instalments, to 45 c.c. of benzene contained in a 500-c.c. round-bottomed flask, with vigorous shaking. Do not allow the temperature of the reaction mixture to exceed 35°, cooling the flask, if necessary, by immersion in cold water. When all the acid has been added, attach a reflux water condenser and heat the mixture to 60° by immersion in warm water. Maintain at this temperature for one hour, shaking occasionally.

Now cool the contents of the flask, and add 50 c.c. of water. Separate off the lighter, oily layer of nitrobenzene and wash it first with water, then with dilute caustic soda solution, and again with water. Note that the nitrobenzene will form the lower layer during the washings, as it has a density of 1·21. Dry the separated nitrobenzene by the addition of anhydrous calcium chloride and allow it to stand for twelve hours. Pour off the dried oil into a small flask and distil, using a naked flame and a long air condenser. Collect at 206–210°. Yield, 50 gm.

Nitrobenzene is a pale yellow oil with an odour of bitter almonds. It is miscible with benzene in all proportions. It is very soluble in alcohol and ether, but only slightly soluble in water. $\Delta = 1{\cdot}2116$ (13°). M.P. = 5°; B.P. = 209°. For tests, see paragraph **320.**

Preparation 63. *m*-DINITROBENZENE, $C_6H_4 \cdot (NO_2)_2$.

175. Reaction.—As shown in paragraph **172**, dinitration is not so easily effected as mononitration, and the principal product is the meta-dinitro compound. Dinitration is carried out, therefore, at a somewhat higher temperature, and with a mixed acid containing less water. In this preparation a mixture of concentrated sulphuric acid and fuming nitric acid is usually employed, but it is quite as satisfactory to use a mixture of fuming sulphuric acid and strong nitric acid (Δ 1·42).

"*Pure nitric acid*" ($\Delta = 1{\cdot}42$) contains about 70 per cent. HNO_3, and thus 1 c.c. = 1 gm. HNO_3 approximately.

"*Fuming nitric acid*" ($\Delta = 1{\cdot}50$) contains about 94 per cent. HNO_3 (see paragraph **507**).

176. Preparation.—Carefully mix in a small round-bottomed flask, 20 c.c. of fuming nitric acid ($\Delta = 1{\cdot}5$) and 20 c.c. of concentrated sulphuric acid. Add 15 c.c. of nitrobenzene in four instalments with shaking, and then warm on the water bath to 100° for one hour. Whilst hot pour the whole into 300 c.c. of cold water. Filter off the precipitated dinitrobenzene and wash well with cold water. Recrystallise from diluted methylated spirit. Yield, 20 gm.

***m*-Dinitrobenzene** crystallises in long, colourless needles from alcohol. It is odourless and practically insoluble in cold water, but is very soluble in alcohol, ether and benzene. M.P. = 90°; B.P. 297°. For tests, see paragraph **319**.

PREPARATION 64. ***o-* and *p*-NITROPHENOL,** $C_6H_4 . (OH) . NO_2$.

177. Reaction.—When phenol is nitrated in aqueous solution with dilute nitric acid, a 50 per cent. yield is obtained, considerable quantities of tarry compounds being simultaneously produced (**172**). It should be noticed that the presence of the phenolic group greatly facilitates nitration, so much so that phenol itself can be nitrated at 20° with 20 per cent. aqueous nitric acid. Nitration in solution in glacial acetic acid gives almost quantitative yields, without tar.

Owing to the formation of tarry products very few nitro-derivatives of phenols are prepared commercially except by indirect methods. For instance, dinitrophenol is obtained by the action of alkalies on chlor-dinitrobenzene:

$$C_6H_3 . Cl . (NO_2)_2 + NaOH \rightarrow C_6H_3 . (OH) . (NO_2)_2 + NaCl$$

The ortho- and para-nitrophenols may be readily separated by steam-distillation, the ortho-derivative being easily volatile in steam. The mononitration of phenol yields approximately 59 per cent. of the ortho-, 38 per cent. of the para-, and 3 per cent. of the meta-compound.

178. Preparation.—Dissolve separately 31 gm. of phenol in 70 c.c. of glacial acetic acid, and 21 c.c. of pure nitric acid ($\Delta =$ 1·42) in 30 c.c. of glacial acetic acid. Place the phenol solution in a beaker, and run in the nitric acid solution *slowly* from a tap funnel so that the reaction mixture maintains a temperature of

between 25° and 30° C. Stir during the addition with a thermometer. When all the nitric acid has been added allow to stand for one hour.

Now steam-distil the mixture until no more of the volatile ortho-derivative distils over. If the ortho-compound solidifies in the condenser, stop the flow of cold water into the condenser until the nitro-body has melted out. The para-compound remains in the distillation flask, and the ortho-compound forms a solid mass in the receiver.

NOTE.—A somewhat better yield is obtained by first *nearly* neutralising the acetic acid present in the distillate. A strong solution of caustic soda should be added as long as the solution does not deepen in colour. The nitrophenol present, being pseudo-acidic, and forming highly coloured salts, acts as an indicator.

Filter off the ortho-nitrophenol from the cold distillate and recrystallise it from dilute methylated spirit at a temperature not exceeding 45°. Yield, 24 gm.

Add a strong solution of caustic soda to the mixture remaining in the distilling flask, to convert the para-nitrophenol present into the soluble salt. About 5 gm. of caustic soda will be required. Evaporate the solution to a bulk of 200 c.c., and filter through glass wool or asbestos placed on a Buchner funnel. When cold acidify the filtrate with concentrated hydrochloric acid. Dissolve the precipitated solid in moderately strong hydrochloric acid solution and boil with good animal charcoal. Filter and allow the solution to cool, when the para-derivative will crystallise out. In recrystallising it must be remembered that although it melts when dry at 114° C., yet under water its melting-point is 48° C. Yield, 12 gm.

o-**Nitrophenol** crystallises in yellow needles, with a peculiar and characteristic smell. It is steam-volatile, easily soluble in alcohol, ether, acetic acid and alkalies (red solution); only sparingly soluble in water. M.P. = 45·2°; B.P. = 214°. For tests, see paragraph **319.**

p-**Nitrophenol** crystallises in long colourless needles. It is odourless and not volatile in steam. Easily soluble in alcohol, ether, acetic acid and alkalies (yellow solution). Moderately soluble in hot water. M.P. = 114° C., and 48° C. under water. Boils at 280° C., with some decomposition. For tests, see paragraph **319.**

PREPARATION 65. *o*- **and** *p*-**NITRANILINE,** $C_6H_4 . (NO_2) . NH_2$.

179. Reaction.—The nitranilines can be prepared either by the partial reduction of the dinitrobenzenes with alkaline sulphides

(paragraph **194**), or by the nitration of aniline and its derivatives. The ortho- and para-compounds are prepared by the latter method and the meta-compounds by the former.

It is necessary to protect the amino-group before nitration. This is usually done by acetylation, although technically other methods are also used, *e.g.*, the aniline is converted into benzylidene aniline, which is then nitrated and hydrolysed, the benzaldehyde being subsequently recovered by steam-distillation.

$$C_6H_5 . NH_2 + C_6H_5 . CHO \xrightarrow{50^\circ} C_6H_5 . N = CH . C_6H_5 + H_2O$$

$$C_6H_5 . N = CH . C_6H_5 + HNO_3 \xrightarrow{H_2SO_4}$$
$$p\text{-}C_6H_4 . (NO_2) . N = CH . C_6H_5 + H_2O$$

$$p\text{-}C_6H_4(NO_2)N = CH . C_6H_5 + H_2O \xrightarrow{100^\circ} p\text{-}C_6H_4(NO_2)NH_2 + C_6H_5 . CHO$$

The remarkable directive influence of the solvent during the nitration of anilides is discussed in paragraph **172**.

180. Preparation.—Dissolve 30 gm. of finely powdered acetanilide in 40 c.c. of concentrated sulphuric acid, not allowing the temperature to exceed 35°. Slowly add, with stirring, a mixture of 25 c.c. of concentrated nitric acid ($\Delta = 1{\cdot}42$), and 25 c.c. of strong sulphuric acid, keeping the temperature between 35°–40°. Leave over night, and then pour into 150 c.c. of water, to precipitate the yellow nitro-acetanilides. Heat the whole on a vigorously boiling water bath until complete solution takes place, when the anilides will be hydrolysed by the diluted acid. The operation takes about two hours.

Cool the solution to 40–50°, and pour on to 200 gm. of crushed ice, whereby the feebly basic ortho-nitraniline is precipitated, whilst the more strongly basic para-compound will remain dissolved in the dilute acid. Filter off the ortho-derivative, and recrystallise from dilute methylated spirit. Yield, 10 gm.

Free the para-derivative from the acid mother-liquor by making alkaline with caustic soda, not allowing the temperature to exceed 40°. Filter off the precipitated nitraniline and recrystallise from dilute methylated spirit. Yield, 30 gm.

***o*-Nitraniline** crystallises in orange needles from alcohol. It is easily soluble in alcohol and ether, but very slightly soluble in water. M.P. = 71·5°. For tests, see paragraph **319**.

***p*-Nitraniline** crystallises in yellow needles from dilute alcohol. It is soluble in alcohol and ether, and is also soluble in 50 parts of hot water and in 1,000 parts of cold water. M.P. = 146·5°. For tests, see paragraph **319**.

AMINES

181. Primary, Secondary and Tertiary Aliphatic Amines.

(i.) *Primary aliphatic amines* are best obtained by the disruption of acid amines with hypochlorites or hypobromites, by the *Hofmann Reaction :*

$$R . CO . NH_2 + NaBrO \rightarrow NaBr + CO_2 + R . NH_2$$

(see methylamine hydrochloride, paragraph **184**).

(ii.) *Secondary aliphatic amines* are most conveniently prepared by boiling the nitrosodialkylanilines with aqueous alkalies :

$$KOH + ON . C_6H_4 . N(CH_3)_2 \rightarrow ON . C_6H_5 . OK + (CH_3)_2 : NH$$

(see diethylamine, paragraph **186**).

(iii.) *Tertiary aliphatic amines* are obtained when alkyl halides are heated with alcoholic ammonia under pressure :

$$NH_3 + CH_3I \rightarrow CH_3NH_2 . HI \rightarrow (CH_3)_2NH . HI \rightarrow (CH_3)_3N . HI \rightarrow (CH_3)_4 . N . I$$

The primary and secondary amines can be removed by interaction with diethyl oxalate, and the unattacked tertiary amine distilled off.

Secondary and tertiary amines are also obtained by the action of dimethyl sulphate (see caution, paragraph **147**) on primary or secondary amines :

$$CH_3 . NH_2 + (CH_3)_2 . SO_4 \rightarrow (CH_3)_2 . NH + CH_3 . HSO_4$$
$$(CH_3)_2 . NH + (CH_3)_2 . SO_4 \rightarrow (CH_3)_3 . N + CH_3 . HSO_4$$

182. Primary Aromatic Amines are best prepared by :

(i.) *The complete reduction of nitro- and nitroso-compounds.* This reaction is usually carried out with nascent hydrogen formed by the interaction of a metal and an acid :

$$ArNO_2 + 6H \rightarrow ArNH_2 + 2H_2O$$

Commercially, iron and water, and a trace of hydrochloric acid, are used to effect the reduction :

$$9Fe + 4H_2O + 4ArNO_2 \rightarrow 4ArNH_2 + 3Fe_3O_4$$

(see aniline, paragraphs **188–191**) ;

or (ii.) *By the reduction of azo-compounds.* This method is particularly useful for the preparation of diamino-compounds and the aminophenols :

$$C_6H_5 . N = N . C_6H_4OH + 4H \rightarrow C_6H_5 . NH_2 + NH_2 . C_6H_4 . OH$$

Aminophenols are also readily obtained by the reduction of the nitrophenols with sodium hydrosulphite.

$$HO \cdot C_6H_4 \cdot NO_2 + \underset{\text{Sodium hydrosulphite}}{3Na_2S_2O_4} + H_2O \rightarrow HO \cdot C_6H_4 \cdot NH_2 + \underset{\text{Sodium metabisulphite}}{3Na_2S_2O_5}$$

(see para-aminophenol, paragraph **192**).

(iii.) *The partial reduction of dinitro-compounds to yield the nitranilines* is accomplished by the agency of alcoholic ammonium sulphide, or better, with sodium polysulphide:

$$C_6H_4(NO_2)_2 + Na_2S_2 + H_2O \rightarrow NO_2 \cdot C_6H_4 \cdot NH_2 + Na_2S_2O_3$$

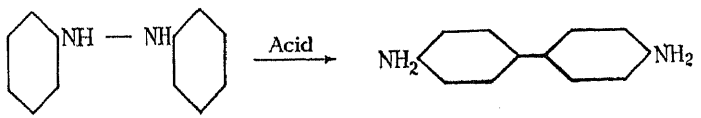
(see meta-nitraniline, paragraph **194**).

(iv.) *Naphthols and polyhydric phenols are readily converted to the corresponding amines by heating with ammonia under pressure.* This method is of the greatest importance in the preparation of β-naphthylamine, since it is not possible to prepare β-nitro-derivatives of naphthalene:

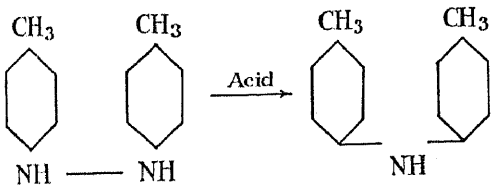
$$C_{10}H_7OH + NH_3 \rightarrow C_{10}H_7NH_2 + H_2O$$

(see β-naphthylamine, paragraph **196**).

(v.) *The hydrazo-compounds are converted into the benzidine derivatives by treatment with acid.* This process is a case of molecular rearrangement:



The amino-groups take the para-position to the diphenyl linkage. If the para-positions are occupied, the ortho- or para-position is taken with the production of an aminodiarylamine. This is known as the semidine change:



(see benzidine, paragraph **198**).

183. Secondary and Tertiary Aromatic Amines are obtained by heating together under pressure :

(i.) The primary aromatic amine and an alkyl halide :

$$C_6H_5 . NH_2 + CH_3I \rightarrow C_6H_5 . NH(CH_3) . HI$$

(ii.) The hydrochloride of the primary aromatic amine and an alcohol, the alkyl halide being formed *in situ* :

$$C_6H_5 . NH_2 . HCl + CH_3OH \rightarrow C_6H_5 . NH . (CH_3) . HCl + H_2O$$

(iii.) The primary aromatic amine and an aromatic halide in the presence of copper powder as a catalyst, and an alkali carbonate :

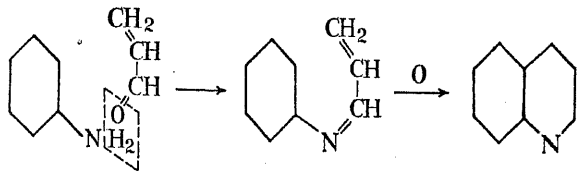
$$2C_6H_5NH_2 + 2C_6H_5Br + Na_2CO_3 \xrightarrow{Cu} 2(C_6H_5)_2NH + 2NaBr + CO_2 + H_2O$$

(iv.) The hydrochloride of the primary aromatic base and the primary amine :

$$C_6H_5 . NH_2 . HCl + C_6H_5NH_2 \rightarrow (C_6H_5)_2 . NH + NH_4Cl$$

(see dimethylaniline, paragraph **200**, and diphenylamine, paragraph **202**).

(v.) *Tertiary amines of the quinoline series* are obtained by heating a primary aromatic amine, which has an unoccupied ortho-position, with glycerol, strong sulphuric acid and an oxidising agent, such as nitrobenzene or arsenic acid. This is known as **Skraup's synthesis :**



The acrolein is produced by the action of the strong sulphuric acid on the glycerol (see quinoline, paragraph **204**).

PREPARATION 66. **METHYLAMINE HYDROCHLORIDE,** $CH_3 . NH_2 . HCl$.

184. Reaction.—The disruption of acid amides by hypobromites or hypochlorites yielding amines is of great importance, and is known as *Hofmann's Reaction.* The reaction takes place in several distinct stages. The halogen first replaces one of the hydrogen atoms of the amido-group :

$$CH_3 . CONH_2 + Br_2 \rightarrow CH_3 . CO . NH . Br + KBr + H_2O$$

The monobrom-derivative thus formed is decomposed by the alkali present, with the formation of an alkyl *iso*-cyanate :

$$CH_3 . CO . NHBr + KOH \rightarrow CH_3 . N = CO + KBr + H_2O$$

which *iso*-cyanate, being unstable in the presence of alkali, decomposes immediately, thus :

$$CH_3 . N = CO + H_2O \rightarrow CH_3 . NH_2 + CO_2$$

This reaction is of general application, and technically, in the course of the synthesis of indigo, anthranilic acid is prepared in this way from phthalimide.

185. Preparation.—Place 25 gm. of acetamide in a 500-c.c. round-bottomed flask, and add 23 c.c. of bromine. Immerse the flask in cold water and carefully add a cold solution of 40 gm. of caustic potash in 300 c.c. of water until the colour of the bromine is almost discharged. The contents of the flask must be kept cold during the addition of the caustic potash. Now pour the reaction mixture slowly into a litre distilling flask containing a warm solution of 75 gm. of caustic potash dissolved in 130 c.c. of water, maintaining the temperature between 60–75° throughout the addition, cooling if necessary. Maintain the temperature at about 70° until the solution is completely decolorised.

Attach the distilling flask to a water condenser, fitted with an adapter which dips just below the surface of a solution of 70 c.c. of concentrated hydrochloric acid and 40 c.c. of water. Add a few pieces of porous pot to the solution in the flask and gently distil, over a wire gauze, until the distillate is no longer alkaline to litmus. Transfer the resultant solution of the amine hydrochloride to a porcelain dish and evaporate nearly to dryness over a naked flame, and, finally, to complete dryness, over the water bath. Powder the residue of methylamine hydrochloride and ammonium chloride, and extract with several small quantities of boiling absolute alcohol, in which reagent the ammonium salt is insoluble. On cooling the combined alcoholic extracts, the methylamine hydrochloride crystallises out. Yield, 20 gm.

Methylamine Hydrochloride crystallises in large, deliquescent tablets, which are soluble in alcohol but insoluble in chloroform. M.P. 226°. For tests, see paragraph **346**.

Preparation 67. **DIETHYLAMINE**, $(C_2H_5)_2 : NH$.

186. Reaction.—The aliphatic secondary amines are most conveniently obtained by the decomposition of the nitrosodialkyl-

anilines by boiling with aqueous alkalies. Nitrosophenols are simultaneously produced:

$$ON \cdot C_6H_4 \cdot N(C_2H_5)_2 + KOH \rightarrow ON \cdot C_6H_4 \cdot OK + (C_2H_5)_2 : NH$$

187. Preparation.—Fit a litre bolt-head flask with a dropping funnel and connect the flask with an efficient water condenser and an adapter which leads into a receiver immersed in ice. Place in the flask a solution of 100 gm. of caustic soda in 250 c.c. of water. Heat the solution almost to boiling over a wire gauze. Run in slowly a solution of 80 gm. of para-nitrosodiethylaniline hydrochloride dissolved in the smallest possible quantity of hot water. This solution should be added at such a rate that the heat of the reaction causes the mixture to boil gently. When all has been added, continue boiling for ten minutes. Fractionally distil from a water bath, the product collected in the receiver, using a small fractionating column, and collect the portion that passes over below 60° C. To this distillate add several pieces of solid caustic potash, allow to stand for several hours in a well-stoppered bottle and redistil. B.P. = 55–56°. Yield, 20 gm.

The main residue in the bolt-head flask contains para-nitrosophenol. Filter through glass wool or asbestos, and acidify the filtrate with concentrated hydrochloric acid. When cold filter off the nitrosophenol and purify it as described in paragraph **169.**

Diethylamine is a volatile, colourless liquid with an ammoniacal odour. It is basic and very soluble in water. $\Delta = 0{\cdot}712$ (15°); B.P. = 55·5°. For tests, see paragraph **332.**

Preparation 68. **ANILINE,** $C_6H_5 \cdot NH_2$.

188. Reaction.—The laboratory process for the reduction of an aromatic nitro-compound to the corresponding amine is frequently carried out by the action of tin and hydrochloric acid. This is an extravagant process, owing to the high cost of the metal, and because considerable quantities of alkali are needed to liberate the base formed. In preparation 69 a much more economical process is given.

189. Preparation.—Fit a litre, round-bottomed flask with an air condenser and place in the flask 60 gm. of granulated tin and 35 gm. of nitrobenzene. Pour through the condenser 120 c.c. of concentrated hydrochloric acid, adding about 15 c.c. at a time. Shake vigorously after each addition. When active ebullition takes place cool the flask by immersing it in cold water. Towards the end of the reduction larger quantities of acid may be added at a time.

When all the acid has been added, warm the flask on the water bath for one hour.

To the warm solution add 100 c.c. of water, and then steam-distil to remove any unchanged nitrobenzene. Disconnect and add a solution of 100 gm. of caustic soda dissolved in 150 c.c. of water and cool the flask, if necessary, to prevent the solution boiling. More caustic soda must be added if any precipitated stannic oxide remains undissolved. Again steam-distil to obtain the aniline. Saturate the distillate with salt and extract twice with ether. Dry the combined ethereal extracts with solid caustic potash, distil off the ether from a water bath and distil the residual aniline from a small flask, using an air condenser and collect the fraction 182–185° C. Yield, 22 gm.

Aniline is a colourless, oily liquid which rapidly darkens in colour on keeping. It is highly refractive, possesses a peculiar odour, and is miscible with alcohol and ether. It is soluble in acids and to the extent of 3·1 per cent. at 16° in water. $\Delta = 1{\cdot}025$ (15°); B.P. = 184·4°. For tests, see paragraph **332**.

Preparation 69. **ANILINE**, $C_6H_5 . NH_2$.

190. Reaction.—The reduction of aromatic nitro-compounds to the corresponding amines is nearly always carried out commercially by the use of iron and water in the presence of a very small quantity of hydrochloric acid. This method should be contrasted with the one given in the previous preparation (paragraph **189**).

The reaction, which is strongly exothermic, is allowed to take place at about 90° C., although in the reduction of α-nitronaphthalene and its derivatives it is inadvisable to let the temperature pass 50° C., or else over-reduction takes place, with evolution of ammonia.

The reduction of the nitro-derivatives takes place in accordance with the equation :

$$9Fe + 4H_2O + 4ArNO_2 \xrightarrow{HCl} 4ArNH_2 + 3Fe_3O_4$$

191. Preparation.—In a round-bottomed flask, fitted with an air condenser, shake together 30 gm. of iron powder, 50 c.c. of hot water and a few drops of nitrobenzene. Add 3 c.c. of concentrated hydrochloric acid, and then little by little, 20 c.c. of nitrobenzene, with vigorous shaking. Cool the flask by immersion in water so that the temperature remains between 80° and 90°. When all the nitrobenzene has been added, warm on the water bath for half an hour, and steam-distil to obtain the aniline. Purify the collected

aniline as in the previous preparation (paragraph **189**). Yield, 17 gm.

PREPARATION 70. ***p*-AMINOPHENOL,** $HO . C_6H_4 . NH_2$.

192. Reaction.—The reduction of such compounds as the nitrophenols to the aminophenols is very conveniently carried out by the use of sodium hydrosulphite, which is added to the boiling alkaline solution of the nitrophenol until the brilliant colour of the solution is just discharged. When sodium hydrosulphite acts as a reducing agent it is itself oxidised to a meta-bisulphite, thus :

$$HO . C_6H_4 . NO_2 + H_2O + 3Na_2S_2O_4 \rightarrow HO . C_6H_4 . NH_2 + 3Na_2S_2O_5$$

193. Preparation.—Dissolve 28 gm. of para-nitrophenol and 10 gm. of caustic soda in 120 c.c. of water. Boil the solution very gently and dust in powdered sodium hydrosulphite until the solution loses its bright colour. Add a little good animal charcoal, boil five minutes, and filter through a previously warmed Buchner funnel. The filtrate on cooling deposits the aminophenol as a mass of colourless crystals. Filter off, wash with cold water, and dry in a vacuum desiccator. Yield, 18 gm.

The ortho-derivative may be prepared similarly from ortho-nitrophenol.

***p*-Aminophenol** crystallises in white scales that readily turn brown on exposure. It is slightly soluble in water and moderately soluble in alcohol. M.P. = 184°, with decomposition. For tests, see paragraph **331**.

***o*-Aminophenol** crystallises and sublimes in white scales that readily turn brown. It is slightly soluble in water, moderately so in alcohol, and readily in ether. M.P. = 170°. For tests, see paragraph **331**.

PREPARATION 71. ***m*-NITRANILINE,** $NO_2 . C_6H_4 . NH_2$.

194. Reaction.—The reduction of one of two nitro-groups present in an aromatic compound is effected by the use of alcoholic ammonium sulphide, or more economically by using boiling solutions of the alkaline polysulphides. The dinitro-derivative is boiled with sodium sulphide and an excess of sulphur. It is most important that the dinitrobenzene should be pure.

$$C_6H_4(NO_2)_2 + Na_2S_2 + H_2O \rightarrow NO_2 . C_6H_4 . NH_2 + Na_2S_2O_3$$

195. Preparation.—Place 25 gm. of recrystallised *m*-dinitrobenzene and a litre of water in a large flask and gently boil over a wire gauze until solution is complete. To the flask slowly add,

with vigorous shaking, a solution of 10 gm. of sulphur and 40 gm. of sodium sulphide in 150 c.c. of water. Add this mixture at such a rate that the heat of reaction keeps the mixture boiling. Boil gently for one hour, and filter hot by suction to remove precipitated sulphur. The *m*-nitraniline crystallises out from the filtrate on cooling. Filter off the product, wash with cold water and recrystallise from dilute methylated spirit. Yield, 18 gm.

m-**Nitraniline** crystallises in flat, orange-yellow needles from dilute alcohol. It is easily soluble in alcohol and ether, but with difficulty in water. M.P. = 114°. For tests, see paragraph **331**.

PREPARATION 72. β-NAPHTHYLAMINE, $C_{10}H_7NH_2$.

196. Reaction.—Polyhydric phenols and naphthols are readily converted into amino-compounds by heating with ammonia under pressure, particularly in the presence of ammonium sulphite. Since the reaction is reversible, an excess of ammonia must be used :

$$C_{10}H_7OH + NH_3 \rightleftharpoons C_{10}H_7NH_2 + H_2O$$

This method is always used for the manufacture of β-naphthylamine, since it is not possible to nitrate naphthalene and its derivatives in the β-position.

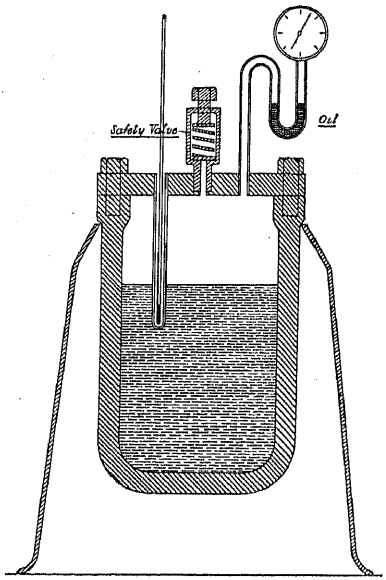
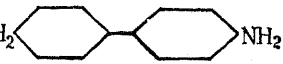


FIG. 26.—Autoclave.

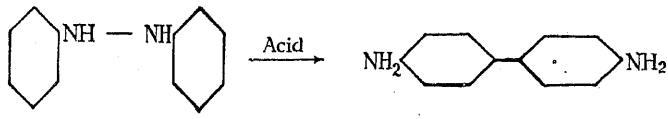
197. Preparation.—Heat together in a small autoclave (Fig. 26) a mixture of 50 gm. of β-naphthol, 50 gm. of ammonium sulphite, 250 c.c. of water and 80 c.c. of concentrated ammonia solution (Δ. = 0·88), to a temperature of 140° for six hours.

After cooling, open the autoclave and filter off the β-naphthylamine. Wash the product with a little cold caustic soda solution to remove β-naphthol and recrystallise from dilute methylated spirit, with the addition of a little good animal charcoal. Yield, 40 gm.

β-**Naphthylamine** crystallises in white, odourless scales. It is soluble in alcohol, ether and ligroin, but almost insoluble in cold water. M.P. = 110°; B.P. = 304°. For tests, see paragraph **331**.

PREPARATION 73. **BENZIDINE,** 

198. Reaction.—The hydrazo-compounds, under the influence of acid, undergo a peculiar molecular rearrangement, known as the *Benzidine Change.*



The amino-groups take the para-positions to the diphenyl linkage. If the para-positions are already occupied, a semidine derivative is obtained, as described in paragraph **182** (v.).

199. Preparation.—Shake together for half an hour a mixture of 10 gm. of hydrazobenzene and 250 c.c. of normal hydrochloric acid, maintaining a temperature of 25–30°. Now warm to 50° and add a little warm water to redissolve any benzidine hydrochloride, and filter hot. To the cold filtrate add an excess of strong caustic soda solution and filter off the precipitated benzidine from the cold solution. Recrystallise the product from very dilute methylated spirit. Yield, 8 gm.

Benzidine crystallises in colourless, lustrous scales from water, which darken in air. It is soluble in alcohol, and soluble to the extent of 1 per cent. in hot water. M.P. = 127°; B.P. = 405°. For tests, see paragraph **331.**

PREPARATION 74. **DIMETHYLANILINE,** $C_6H_5 . N(CH_3)_2$.

200. Reaction.—By heating together a primary amine, its hydrochloride and an alcohol, a secondary or tertiary amine is produced, due to the intermediate formation of the alkyl chloride (paragraph **183** (iv.)).

$$C_6H_5NH_2.HCl + 2CH_3OH \rightarrow C_6H_5.N(CH_3)_2 + HCl + 2H_2O$$

The mixed product is best purified by the use of acetic anhydride, which reacts only with the unchanged aniline and the monomethylaniline. Separation by fractional distillation is not possible owing to the closeness of the boiling-points of the three substances, *e.g.*, Aniline, B.P. = 184°; Monomethylaniline, B.P. = 195°; Dimethylaniline, B.P. = 193°.

201. Preparation.—Introduce into an autoclave (Fig. 26, page 104), or into a sealed tube, a mixture of 40 gm. of aniline hydrochloride, 10 gm. of aniline, and 50 gm. of methyl alcohol. Heat

together for three hours to a temperature of 180° and then for a further three hours to 240°. When cold, remove the product and make alkaline with concentrated caustic soda solution and steam-distil. Separate off the oily product that distils over and dry with a few pieces of solid caustic potash. Reflux for thirty minutes the dried product with 30 c.c. of acetic anhydride and a few drops of strong sulphuric acid, using an air condenser. Distil the whole through an air condenser. Unchanged acetic anhydride passes over below 150°, and then the unchanged dimethylaniline at 190–195°. Yield, 40 gm.

Dimethylaniline is a colourless liquid with a characteristic and somewhat unpleasant odour. It becomes dark on keeping, and stains the stoppers of the containing bottles blue. It is soluble in alcohol, but almost insoluble in water. B.P. = 193°; Δ = 0·9575 (20°). For tests, see paragraph **332**.

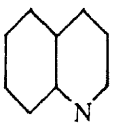
Preparation 75. **DIPHENYLAMINE,** $(C_6H_5)_2 . NH$.

202. Reaction.—Secondary aromatic bases of the type of diphenylamine are prepared by heating together a primary amine and its hydrochloride (**183** (iv.)):

$$C_6H_5NH_2 . HCl + C_6H_5NH_2 \rightarrow (C_6H_5)_2NH + NH_4Cl.$$

203. Preparation.—Heat together in a sealed tube a mixture of 15 gm. of aniline and 30 gm. of aniline hydrochloride for thirty hours to a temperature of 240° C. When cold, extract the product with a boiling solution of *dilute* hydrochloric acid to remove aniline, and then with water. Distil the insoluble residue through an air condenser, collecting between 300–320° C., and finally recrystallise the product from dilute methylated spirit. Yield, 28 gm.

Diphenylamine crystallises in lustrous scales, possessing a faint odour. It is very soluble in alcohol and ether, but almost insoluble in water and dilute acids. M.P. = 54°; B.P. = 302°. For tests, see paragraph **331**.

Preparation 76. **QUINOLINE,** 

204. Reaction.—Quinoline is obtained by heating together aniline, glycerol, strong sulphuric and an oxidising agent such as arsenic acid or nitrobenzene. This is known as **Skraup's synthesis.** The mechanism of the reaction is shown in paragraph **183** (v.).

All aromatic primary amines with an ortho-position to the amino-group unoccupied, react in this way. It is stated that it is always best to use the nitro-compound that corresponds to the amine as the oxidising agent. Thus, with para-toluidine, para-nitrotoluene should be employed.

205. Preparation.—In a large, round-bottomed flask fitted with a reflux condenser, place a mixture of 25 gm. of nitrobenzene, 38 gm. of aniline, 120 gm. of glycerol and 100 gm. of concentrated sulphuric acid. Heat the whole on a sand bath until the reaction sets in, and then quickly raise the flask from the sand bath. When the reaction has moderated replace the flask on the sand bath and reflux gently for three hours. Dilute the dark coloured product with water and steam-distil to remove unchanged nitrobenzene. Add concentrated caustic soda solution to the residue in the flask until strongly alkaline, and again steam-distil to obtain the liberated bases, aniline and quinoline. Separate these from the aqueous layer, dehydrate with solid caustic potash, and reflux with 20 c.c. of acetic anhydride for one hour, in the same way as described for the separation of aniline and dimethylaniline in paragraph **201**. Distil off the excess of acetic anhydride and then the quinoline, collecting the fraction between 235–240°. Yield, 40 gm.

Quinoline is a colourless oil of characteristic and somewhat unpleasant odour. It is miscible with alcohol and ether, but almost insoluble in water. $\Delta = 1{\cdot}095$ (20° C.); B.P. = 236°. For tests, see paragraph **332**.

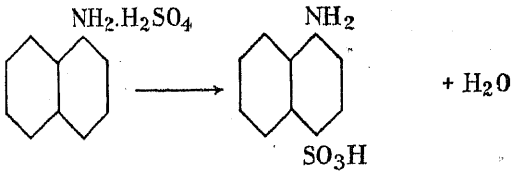
SULPHONIC ACIDS

206. The aromatic sulphonic acids are almost invariably obtained by direct sulphonation, the compound being digested either with strong sulphuric acid, in the presence of a dehydrating agent, such as phosphorus pentoxide or anhydrous potassium sulphate, or with fuming sulphuric acid:

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5 . SO_3H + H_2O$$

The temperature of sulphonation is an important factor in the preparation of naphthalene derivatives. Thus, naphthalene yields the α-compound below 80°, but the β-sulphonic acid above that temperature (see sodium β-naphthalene sulphonate, paragraph **207**).

The sulphonic acids of aromatic amines are obtained by a modification of the above process, in which the sulphate of the base is roasted. The sulphonic group enters the nucleus in the para-position to the amino group:



Thus, naphthionic acid is produced by heating α-naphthylamine sulphate (see sulphanilic acid, paragraph **209**).

PREPARATION 77. SODIUM β-NAPHTHALENE SULPHONATE, $C_{10}H_7 . SO_3Na$.

207. Reaction.—As shown in paragraph **206**, the sulphonation of naphthalene at low temperatures gives rise to the α-compound, but sulphonation at higher temperatures yields principally the β-acid. After sulphonation the sulphonic acids are separated from the excess of sulphuric acid used, by taking advantage of the fact that the calcium, barium and lead salts of sulphonic acids are soluble, whereas the sulphates of these metals are comparatively insoluble. The sodium salts are easily prepared from the calcium sulphonates by double decomposition with sodium carbonate, whereby calcium carbonate is precipitated, and the filtrate yields

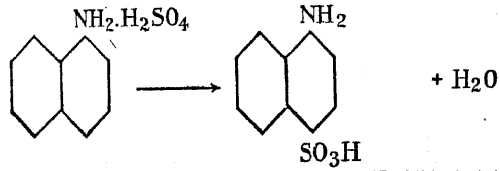
the sodium salt on evaporation. Alkaline fusion of the sodium salts gives rise to the phenols and naphthols (see paragraph **72**).

208. Preparation.—Heat together in an enamelled iron beaker a mixture of 50 gm. of powdered naphthalene and 30 c.c. of concentrated sulphuric acid, maintaining a temperature of 170–180° for eight hours. Pour the cooled mass, with stirring, into 500 c.c. of water, and filter off the unchanged naphthalene. Heat the filtrate to boiling and neutralise by the addition of powdered slaked lime. Filter off the precipitated calcium sulphate and wash the latter with a little water. The filtrate and the washing water are concentrated together by evaporation until a small quantity of the liquid on cooling will deposit crystals of the calcium sulphonate. Now add saturated sodium carbonate solution to the hot liquid until no further precipitation occurs. Filter off the precipitated chalk, and evaporate the filtrate almost to dryness and allow the sodium sulphonate to crystallise out. Yield, 65 gm.

Sodium β-Naphthalene Sulphonate crystallises in white needles, fairly easily soluble in water. The corresponding acid is crystalline and deliquescent, M.P. 161°. For tests, see paragraph **310**.

PREPARATION 78. SULPHANILIC ACID, 

209. Reaction.—By roasting the sulphates of aromatic amines para-amino-sulphonic acids are readily obtained :



α-Naphthylamine Sulphate — Naphthionic Acid

The sulphonic acid group always takes up the para-position to the amino-group.

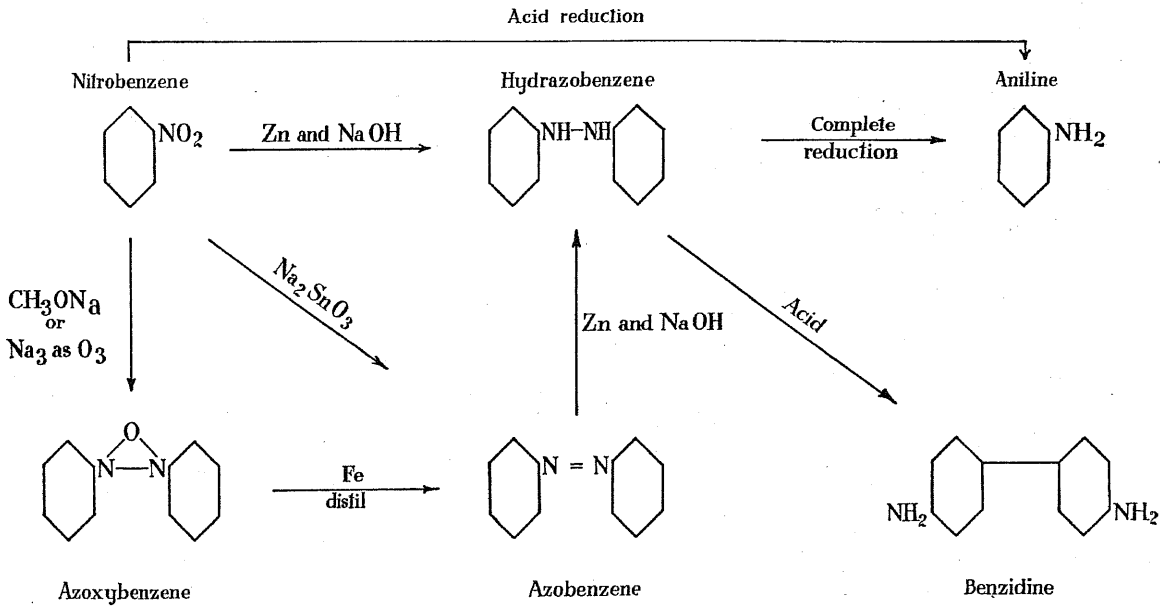
As sulphanilic acid is practically insoluble in cold water, it is very easily isolated.

210. Preparation.—Slowly add, with stirring, 46 gm. of aniline to 28 c.c. of concentrated sulphuric acid contained in a shallow porcelain basin. Heat the whole in an air oven, slowly increasing

the temperature so that it reaches 200° at the end of three hours. Then heat at 210° for five hours. Dissolve the product in boiling water and add powdered caustic soda until just alkaline. This will require about 20 gm. Boil the solution with a little good animal charcoal for ten minutes, and filter hot. Add to the filtrate 100 c.c. of concentrated hydrochloric acid and leave for eight hours. Filter off the precipitated sulphanilic acid on a Buchner funnel, wash with cold water, and dry in an air oven at 110° C. Yield, 60 gm.

Sulphanilic Acid crystallises in colourless rhombic plates, containing two molecules of water of crystallisation, which is driven off at 100°, leaving a white amorphous powder. The hydrated crystals are efflorescent at the ordinary temperature. Soluble in 166 parts of water at 10° C. Decomposes on heating. For tests, see paragraph **354**.

REDUCTION PRODUCTS OF NITROBENZENE



AZOXY-, AZO- AND HYDRAZO-COMPOUNDS

211. Although amines are produced by the vigorous reduction of nitro-compounds, nevertheless, by the use of suitable reducing agents and by the careful control of the reaction, a number of intermediate products may be isolated. The preparation of the more important of these is shown in the scheme on page 111.

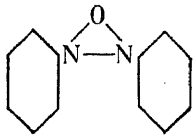
For azoxybenzene, see paragraph **212**; azobenzene, paragraph **214**; hydrazobenzene, paragraph **216**; benzidine, paragraph **198**; and aniline, paragraphs **188–191.**

Also by the reduction of nitro-compounds with zinc dust and hot water, substituted hydroxylamines are produced:

$$C_6H_5 . NO_2 \longrightarrow \underset{\beta\text{-Phenylhydroxylamine}}{C_6H_5 . NHOH}$$

The very important azo-compounds, which can be obtained by the reduction of azoxy-compounds, as shown in the diagram, are also prepared by the "coupling" together of diazonium salts and amines or phenols. In this way the technically important azo-dyes are produced (see paragraphs **218–221**).

PREPARATION 79. **AZOXYBENZENE,**



212. Reaction.—Azoxybenzene is obtained by the moderated reduction of nitrobenzene in alkaline solution. It is probable that nitrosobenzene and β-phenylhydroxylamine are first produced, which, in alkaline solution, readily condense to form azoxybenzene (see paragraph **211**):

$$C_6H_5 . NO_2 \longrightarrow C_6H_5 . NO \longrightarrow C_6H_5 . NHOH$$
$$C_6H_5 . NO + C_6H_5 . NHOH \longrightarrow C_6H_5N . O . NC_6H_5 + H_2O$$

The reduction may be carried out by the use of previously prepared sodium methylate, the latter being oxidised to sodium formate:

$$CH_3 . ONa + O_2 \longrightarrow H_2O + H . COONa$$

This mild reduction process must not be confused with the energetic reduction which is obtained by the addition of sodium to

an alcohol, when the nascent hydrogen liberated acts as a very powerful reducing agent :

$$CH_3OH + Na \rightarrow CH_3ONa + \dot{H}$$

Sodium arsenite solution may also be used for the reduction of the nitrobenzene in the place of the more expensive sodium methylate solution.

213. Preparation.—Reflux together, using a water condenser, a mixture of 30 gm. of nitrobenzene, 36 gm. of arsenious oxide, 50 gm. of caustic soda and 500 c.c. of water. The whole should be heated over a wire gauze for eight hours. Cool and separate the resultant oil, and wash the latter with water three times. Add a little dilute sulphuric acid and steam-distil. A little unchanged nitrobenzene passes over first, and then the azoxybenzene, which is only volatile with difficulty in steam. Filter and recrystallise the product from three times its weight of methyl alcohol, cooling the vessel by means of ice. Yield, 16 gm.

Azoxybenzene crystallises in yellow needles from alcohol. It is easily soluble in alcohol, ether, chloroform and benzene. M.P. = 36·2°. For tests, see paragraph **319**.

Preparation 80. **AZOBENZENE,** $C_6H_5 . N : N . C_6H_5$.

214. Reaction.—The azo-hydrocarbons are best prepared in the laboratory by the distillation of azoxy-compounds with iron filings. Technically they are obtained by the electrolytic reduction of nitro-compounds in aqueous alcohol.

The more important amino-azo and hydroxy-azo compounds are obtained by the " coupling " of diazonium compounds with amines and phenols (see paragraphs **218–221**).

215. Preparation.—Thoroughly dry in the steam oven 15 gm. of azoxybenzene and 45 gm. of iron filings. When dry, thoroughly mix the two substances by grinding, and distil the mixture from a very small retort made by blowing a small bulb at the end of a moderately wide piece of glass tubing, 12–15 c.m. long. To effect the distillation, heat the retort with a small luminous flame kept in constant motion. Towards the end of the reaction a non-luminous flame may be used. Collect the distillate in a small beaker. Wash the distillate with a little dilute hydrochloric acid to remove traces of aniline, and then recrystallise from ligroin, in which it is easily soluble. Yield, 8 gm.

Azobenzene crystallises in orange-yellow plates, which are soluble

in alcohol, ligroin and other organic solvents. M.P. = 68°. For tests, see paragraph **319**.

PREPARATION 81. **HYDRAZOBENZENE,** $C_6H_5 . NH . NH . C_6H_5$.

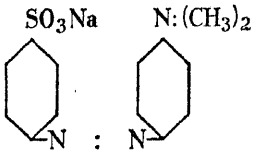
216. Reaction.—The hydrazo-compounds are readily obtained by the moderated reduction of nitro-, nitroso- and azo-compounds in alkaline or neutral medium. Reduction in acid solution would give rise to a benzidine derivative by molecular rearrangement, see paragraph **182** (v).

The reduction of nitro- and azo-compounds to the corresponding hydrazo-derivatives is usually carried out with zinc dust and caustic soda in aqueous-alcoholic solution.

217. Preparation.—Dissolve 10 gm. of azobenzene in 100 c.c. of absolute alcohol contained in a round-bottomed flask and fitted with a reflux water condenser. Add a solution of 4 gm. of caustic soda in 8 c.c. of water and reflux the whole gently over a wire gauze or sand bath. To the boiling solution, add in instalments, zinc dust until the bright coloured solution is decolorised. This will require 15–20 gm. of zinc dust. Filter the hot solution through a Buchner funnel into about 250 c.c. of water containing a very little freshly dissolved sulphur dioxide. Filter off the precipitated hydrazobenzene, wash with a little water containing sulphur dioxide, and dry on a porous plate. Recrystallise the product from diluted methylated spirit. Yield, 8 gm.

Hydrazobenzene crystallises in lustrous, colourless leaflets, which rapidly become orange coloured by oxidation in air. It is practically insoluble in cold water, but moderately soluble in alcohol. M.P. = 126°. For tests, see paragraph **331**.

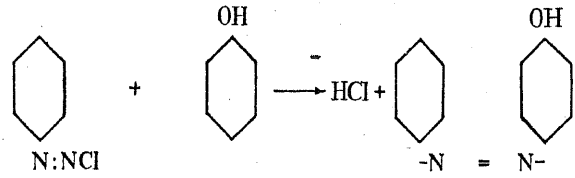
PREPARATION 82. **METHYL ORANGE,**



218. Reaction.—The very important azo-dyes are prepared by the " coupling " of diazonium salts with primary, secondary and tertiary amines or with phenols. The solution of the diazonium salt is either added to a solution of the amine in an acid or to the phenol dissolved in caustic soda solution.

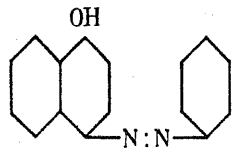
Coupling takes place in the para-position to the amino- or

hydroxyl group. If the para-position is occupied already, then the ortho-position is taken.

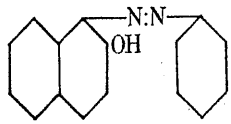


In the case of dihydric phenols and diamino-compounds it is usually only the meta-compounds, such as resorcinol, that will couple to form azo-derivatives.

In the naphthalene series if the amino- or hydroxyl group is in the α-position, then coupling takes place in the para-position.



If the amino- or hydroxyl group is in the β-position, then the azo-group enters into the α-position.



These rules are of general application, although the presence of other groups in the nucleus may affect the position at which coupling takes place, but it should be remembered that in no case will coupling take place in the meta-position.

Methyl orange, or helianthine, is formed by the coupling together of diazotised sulphanilic acid and dimethylaniline:

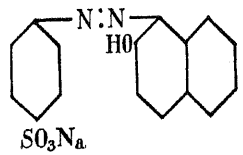
$$2NaOH + SO_3H \cdot C_6H_4 \cdot N : NCl + C_6H_5 \cdot N(CH_3)_2 \rightarrow NaCl + 2H_2O + SO_3Na \cdot C_6H_4 \cdot N : N \cdot C_6H_5 \cdot N(CH_3)_2$$

219. Preparation.—Dissolve 4 gm. of anhydrous sodium carbonate in 150 c.c. of water. Add 12 gm. of sulphanilic acid and warm gently to complete solution. Cool and add a solution of 4·6 gm. of sodium nitrite in 20 c.c. of water. Cool the whole to 5° C. by means of ice, and add very gradually a mixture of 8 c.c. of concentrated hydrochloric acid and 10 c.c. of water, so that the

temperature does not exceed 8° C. To the solution of the diazonium salt thus obtained add a cold solution of 8 gm. of dimethylaniline dissolved in 8 c.c. of strong hydrochloric acid and 25 c.c. of water. Add caustic soda solution until distinctly alkaline, and then add 30 gm. of common salt, in order to "salt out" the methyl orange. Allow to stand for one hour, filter off the product at the pump, wash with a little cold water, and finally recrystallise from boiling water. Yield, 20 gm.

Methyl Orange, or **Helianthine,** is the sodium salt of the sulphonic acid. It is an orange, crystalline powder, which in aqueous solution is yellow, whereas the free acid is intensely red.

PREPARATION 83. **ORANGE II,**



220. Reaction. The mechanism of the interaction of the diazonium salts with phenols and naphthols is described fully in paragraph **218.** Orange II is formed by the coupling together of diazotised sulphanilic acid and β-naphthol.

221. Preparation.—Diazotise 12 gm. of sulphanilic acid exactly as described in the previous preparation. Dissolve 10 gm. of β-naphthol in 100 c.c. of a normal solution of sodium hydroxide and cool to 10° C. Slowly pour the solution of the diazonium salt, with continual stirring, into this solution of β-naphthol, testing from time to time to make sure that the whole is still alkaline in reaction. Add 40 gm. of common salt and leave for one hour. Filter off the precipitated dye on a Buchner funnel, wash with cold water, and dry on a porous plate. Yield, 20 gm.

Orange II is an orange-yellow dye, readily soluble in water and alcohol, but insoluble in ether and benzene. Orange II dyes wool an orange colour from an acid bath.

THE HYDRAZINES

222. The hydrazines are the mono-substituted derivatives of hydrazine of the general formula R . NH . NH_2. Of these the aromatic compounds alone are of importance. The di-substituted derivatives of the type R . NH . NH . R are the hydrazo-compounds, and have already been considered in paragraphs **211** and **216.**

The arylhydrazines are of considerable importance, especially on account of the derivatives they form with aldehydes, ketones and the sugars. The preparation of a phenylhydrazone and of an osazone have been described in paragraphs **110–113.**

These hydrazines are invariably prepared by the reduction of the diazonium compounds. The reducing agents that are most frequently employed are sulphurous acid, stannous compounds, or zinc dust and acetic acid:

$$C_6H_5 . N : NCl + 4H \rightarrow C_6H_5 . NH . NH_2 + HCl$$

(see phenylhydrazine, paragraph **223**).

PREPARATION 84. **PHENYLHYDRAZINE,** $C_6H_5 . NH . NH_2$.

223. Reaction.—Phenylhydrazine is conveniently obtained by the reduction of diazobenzene chloride with stannous chloride:

$$C_6H_5 . N : NCl + 2SnCl_2 + 4HCl \rightarrow C_6H_5 . NH . NH_2 . HCl + 2SnCl_4$$

As phenylhydrazine is poisonous, care must be taken not to inhale the vapour.

224. Preparation.—Diazotise 20 gm. of aniline exactly as described in paragraph **77.** Dissolve 120 gm. of stannous chloride in about 100 c.c. of concentrated hydrochloric acid and cool in ice. Add this solution to the ice-cold solution of diazobenzene chloride and keep the whole surrounded by ice. Leave for one hour. Filter off at the pump the thick white crystalline precipitate of phenylhydrazine hydrochloride.

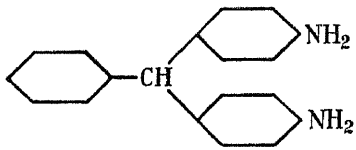
Transfer the product to a flask and shake *thoroughly* with an excess of caustic soda solution in order to set free the base. Extract the liberated base with ether. Dry the ethereal solution with solid potassium carbonate. Distil off the ether from a water bath and distil the residual oil under reduced pressure. Yield, 18 gm.

Phenylhydrazine is a colourless liquid that rapidly turns brown on exposure to the air. It is difficultly soluble in water, but is miscible with alcohol, ether, benzene, and other organic solvents. $\Delta = 1{\cdot}097$ (23° C.); B.P. = 243·5° (with slight decomposition). For tests, see paragraph **332**.

THE TRIPHENYLMETHANE DYES

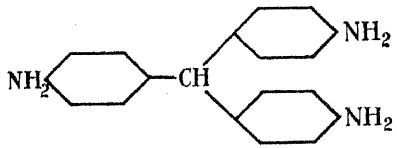
225. The important triphenylmethane dyes may be divided into several classes, of which the following are the more important :—

(i.) **The Malachite Green Group**, derived from p_2-diaminotriphenylmethane :



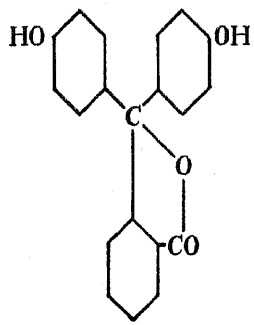
(see malachite green, paragraph **226**).

(ii.) **The Rosaniline Group,** derived from p_3-triaminotriphenylmethane :

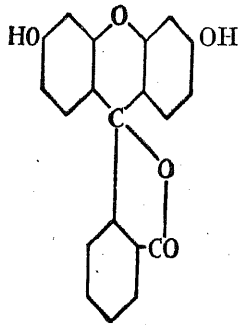


(see magenta, paragraph **228**).

(iii.) **The Phthaleins and Pyronines,** derived from the dihydroxytriphenylmethane carboxylic acids. Thus, phenolphthalein has the structure :



and the pyronines, such as fluoresceïn, have an oxygen linking:



(see phenolphthalein, paragraph **230**, and fluoresceïn, paragraph **232**).

PREPARATION 85. **MALACHITE GREEN,**

$$C_6H_5 . C\begin{matrix} C_6H_4 . N(CH_3)_2 \\ \diagdown\!\!\diagup \\ C_6H_4 : N(CH_3)_2 . Cl \end{matrix}$$

226. Reaction.—Malachite green is formed by the condensation of a molecule of benzaldehyde with two molecules of dimethylaniline. The resulting *leuco* base is then oxidised to the corresponding carbinol, which in the presence of acids at once loses water, with the production of the dyestuff. Condensation is always effected in the para position to the amino-group:

$$C_6H_5 . CHO + 2C_6H_5 . N(CH_3)_2 \xrightarrow{ZnCl_2} H_2O + \underset{\text{Leuco base}}{C_6H_5 . CH : [C_6H_4N(CH_3)_2]_2}$$

$$\xrightarrow{O} C_6H_5 . C . OH(C_6H_4 . N(CH_3)_2)_2 \xrightarrow{HCl} C_6H_5 . C\begin{matrix} C_6H_4 . N(CH_3)_2 \\ \diagdown\!\!\diagup \\ C_6H_4 = N(CH_3)_2 \; Cl \end{matrix}$$

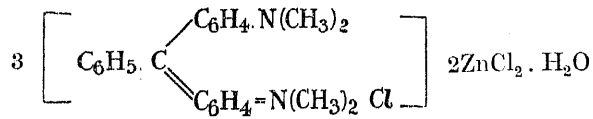
Carbinol — Malachite green

The intense colour of the dyestuff is, of course, due to the formation of the quinonoid nucleus in the last stage of the reaction.

227. Preparation.—Heat for four hours in a porcelain dish placed upon a water bath, a mixture of 20 gm. of benzaldehyde, 50 gm. of dimethylaniline and 20 gm. of powdered, freshly fused, zinc chloride. Dissolve the melt in hot water and transfer the whole to

a large round-bottomed flask and steam-distil until the excess of dimethylaniline has been removed. Cool the flask, when the leuco base solidifies and adheres to the glass. Pour away the aqueous liquid and wash the adherent base with water by decantation. Dissolve out the leuco base with alcohol by warming, and allow it to crystallise out overnight. If the product separates as an oil it must be recrystallised from a less saturated solution. Filter off the crystalline product and dry on a porous plate.

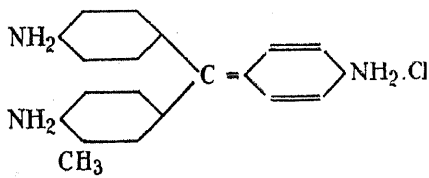
Weigh the product and dissolve it in warm dilute hydrochloric acid, containing *exactly* 2·7 gm. of hydrogen chloride for each 10 gm. of leuco base. Dilute to 700 c.c. and add about 100 gm. of crushed ice. Now slowly add, for each 10 gm. of the leuco base, a thin paste of 7·5 gm. of pure lead peroxide and shake frequently for ten minutes. Add a saturated solution of about 10 gm. of crystallised sodium sulphate and filter off the mixed precipitate of lead sulphate and chloride. To the filtrate add a strong solution containing 8 gm. of zinc chloride for each 10 gm. of base taken, and saturate the whole with common salt. Filter off the dyestuff which is precipitated as a double zinc chloride compound and recrystallise it from a little water and again precipitate by the addition of salt. Filter, and dry on a porous plate. The zinc chloride compound has the formula :



Yield, 65 gm.

Malachite Green (zinc chloride compound) crystallises in yellowish green crystals, easily soluble in water. Malachite green dyes silk and wool directly, but with cotton the material should be previously mordanted with tartar emetic and tannin.

PREPARATION 86. **MAGENTA,**



228. Reaction.—The rosaniline dyes are obtained by the conden

sation of an amine with a para-toluidine in the presence of an oxidising agent :

$$NH_2 . C_6H_4 . CH_3 + 2C_6H_5NH_2 \xrightarrow{O} \underset{\text{Leuco base}}{NH_2 . C_6H_4 . CH : (C_6H_4 . NH_2)_2}$$

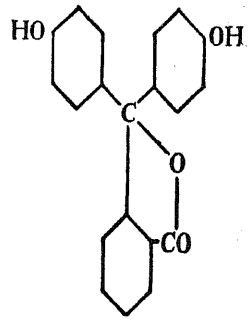
$$\xrightarrow{O} \underset{\text{Carbinol}}{NH_2 . C_6H_4 . COH(C_6H_4 . NH_2)_2} \xrightarrow{HCl} \underset{\text{Dyestuff}}{(NH_2 . C_6H_4)_2C = C_6H_4 = NH_2 . Cl}$$

The leuco base is oxidised to the carbinol, which in the presence of acid loses a molecule of water to form the dyestuff, in a manner analogous to the formation of malachite green (paragraph **226**).

The para-toluidine can be condensed with two molecules of different amines. Thus, rosanilines result from the condensation of para-toluidine with (i.) two molecules of an aniline, or (ii.) two molecules of an ortho-toluidine, or (iii.) one molecule of an aniline and one molecule of an ortho-toluidine. Meta-toluidines do not react in this way. Magenta itself is formed from one molecule of aniline and one molecule of ortho-toluidine condensed with para-toluidine. It is usual to employ either arsenic acid or nitrobenzene in the presence of ferrous chloride as the oxidising agent in the reaction (compare Skraup's synthesis, paragraph **204**).

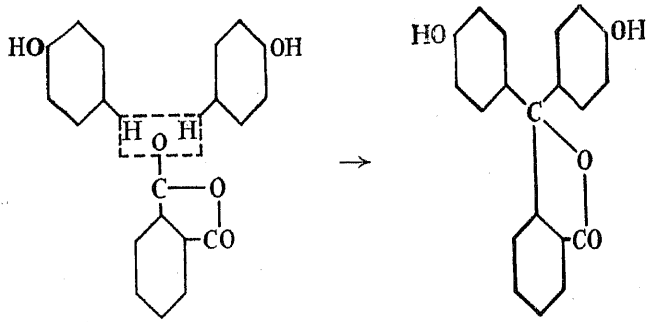
229. Preparation.—In a round-bottomed flask, fitted with an air condenser, place a mixture of 15 gm. of aniline, 20 gm. of ortho-toluidine, 20 gm. of para-toluidine, 30 gm. of nitrobenzene, and 35 gm. of concentrated hydrochloric acid. Heat the whole to 100° C. in an oil bath and slowly add a solution of ferrous chloride, obtained by dissolving 2 gm. of iron powder in the minimum quantity of strong hydrochloric acid. Heat to 190° and maintain at this temperature until a sample withdrawn on a glass rod solidifies on cooling. This will require about six to eight hours. Steam-distil the whole until no more unchanged nitrobenzene or amines pass over. Dilute the residue in the flask with water to 250 c.c., well stir and add concentrated hydrochloric acid until acid in reaction. Add 20 gm. of salt and boil for ten minutes. Cool and pour away the liquid. Dry the solid, brittle green residue, pulverise it, and weigh. Extract the residue with 700 c.c. of boiling water, containing 8 c.c. of concentrated hydrochloric acid. Cool to 65° and filter quickly. To the filtrate add 50 gm. of salt and leave overnight. Filter off the magenta and recrystallise it from boiling water containing a little hydrochloric acid. Yield, 30 gm.

Magenta (fuchsine) forms dark coloured crystals with a green reflex. It is soluble in boiling water and in alcohol, giving a carmine coloured solution, which dyes silk and wool a violet-red colour without a mordant.

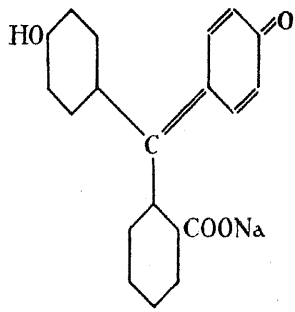


PREPARATION 87. **PHENOLPHTHALEIN,**

230. Reaction.—The phthaleins are obtained by heating together a phenol, phthalic anhydride and a dehydrating agent, such as strong sulphuric acid or zinc chloride :



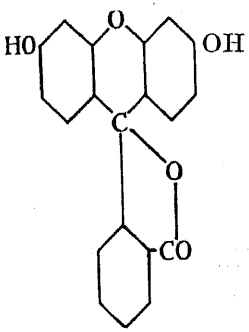
The phthaleins themselves are colourless, but form bright coloured salts, due to the change of structure to the quinonoid form :



231. Preparation.—In a small porcelain dish, partially immersed in an oil bath, heat together a mixture of 15 gm. phthalic anhydride, 30 gm. of phenol, and 15 gm. of concentrated sulphuric acid, for six hours, at 120° C. Pour the mass whilst hot into 300 c.c. of cold water and steam-distil until no more phenol passes over. Cool the contents of the flask and filter off the precipitate, and wash

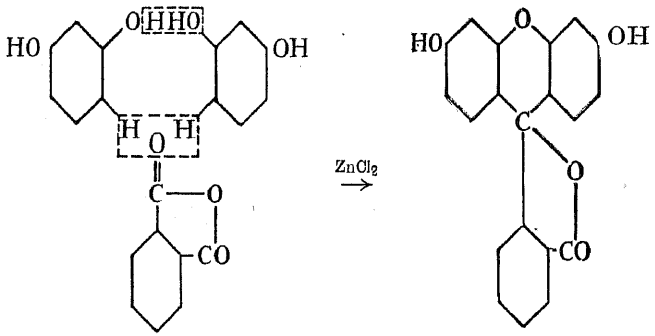
it with cold water. Dissolve the precipitate in a 10 per cent. solution of caustic soda, filter from any undissolved impurity, and acidify the filtrate with dilute hydrochloric acid. Leave overnight and then filter off the precipitated phenolphthalein, and dry by pressing between filter paper. Reflux the product on the water bath for one hour with some good animal charcoal and six times its weight of absolute alcohol. Filter hot and wash the charcoal left on the filter with 20 c.c. of hot absolute alcohol. Distil off nearly half the alcohol and dilute the residue with six times its volume of hot water. Filter quickly through a piece of calico and heat the filtrate on the water bath to drive off the alcohol. Cool and allow the phenolphthalein to crystallise out. Filter off and dry on a porous plate. Yield, 8 gm.

Phenolphthalein occurs as a white crystalline powder. It is soluble in alcohol, with some difficulty in ether, and is almost insoluble in water. Dissolves in alkalies, giving an intensely red colour. M.P. 250–253°.



PREPARATION 88. **FLUORESCEÏN,**

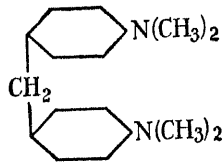
232. Reaction.—The pyronines differ from the phthaleins in that they contain a bridged oxygen linking. They are formed by the condensation of phthalic anhydride and a meta-dihydric phenol, such as resorcinol :



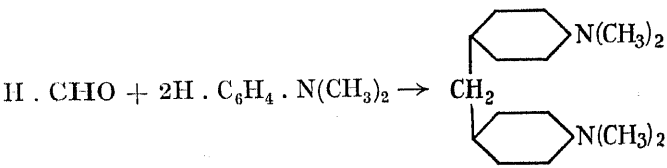
233. Preparation.—Heat together in a nickel dish or crucible, immersed in an oil bath, a finely ground mixture of 12 gm. phthalic anhydride and 18 gm. resorcinol. When the temperature reaches 180° C. stir in slowly 10 gm. of finely powdered, anhydrous zinc chloride. Increase the temperature to 210° and continue to heat at this temperature for two hours. Cool, and chip out the solid mass. Finely powder the product and boil it for ten minutes with a mixture of 180 c.c. of water and 20 c.c. of strong hydrochloric acid. Filter off the fluoresceïn and boil it with 25 c.c. of absolute alcohol to remove impurities. Filter and dry on a porous plate. Yield, 25 gm.

Fluorescein is a yellow-orange powder. It is insoluble in cold water; soluble with difficulty in alcohol and ether; soluble in strong sulphuric acid; soluble in alkalies, giving a yellowish red solution with intense greenish yellow fluorescence.

PREPARATION 89. **TETRAMETHYL-*p*,*p*-DIAMINO-DIPHENYLMETHANE,**



234. Reaction.—Substituted derivatives of diphenylmethane which are used as intermediates for the manufacture of dyes of the triphenylmethane class, are prepared by the condensation of amines with formaldehydes:



Formaldehyde is one of the most important intermediates in the commercial manufacture of dyestuffs.

235. Preparation.—Mix together in a round-bottomed flask 24 gm. of pure dimethylaniline, 15 c.c. of water and 26 gm. of 30 per cent. hydrochloric acid. Immerse the flask in warm water and maintain it at a temperature of 30°, then slowly add 80 gm. of a 40 per cent. solution of formaldehyde. The strength of the formaldehyde solution must have been determined by titration

(see *Note* below). Heat to 85° and maintain this temperature for five hours, stirring occasionally. Cool the product and precipitate the base by the addition of about 9 gm. of caustic soda dissolved in a very little water. Cool to 15°, filter and wash the product with water. Recrystallise from alcohol and dry on a porous tile. Yield, 25 gm.

Tetramethyl-*p*,*p*-diaminodiphenylmethane crystallises in colourless, lustrous leaflets. Almost insoluble in water; sparingly soluble in cold alcohol; easily soluble in ether and mineral acids. It is a tertiary amine and is coloured emerald green by the addition of a trace of iodine. M.P. 90–91°.

NOTE.—**Estimation of Formaldehyde.**—Ten cubic centimetres of the formalin solution, approximately 40 per cent. formaldehyde, are diluted to 400 c.c. and 5 c.c. taken for the estimation. To this are added 40 c.c. of a decinormal solution of iodine, and then a 20 per cent. solution of sodium hydroxide, drop by drop, until the liquid becomes light yellow in colour. After standing fifteen minutes the solution is just acidified with hydrochloric acid and the excess of iodine titrated with a decinormal solution of sodium thiosulphate:

$$H.CHO + I_2 + 2NaOH \longrightarrow 2NaI + H_2O + H.COOH$$

Hence, 1 c.c. of decinormal iodine absorbed is equivalent to 0·0015 gm. of formaldehyde.

SECTION III

QUALITATIVE ANALYSIS

250. Introductory Remarks.—It should be the aim of the student to undertake the analysis of an organic substance with as much care as is taken in the detection of an inorganic salt. Too frequently the student, who is commencing organic analysis, is unduly influenced by obvious physical properties such as odour, colour and boiling-point. A series of arbitrary tests are then made until by chance the compound is identified.

In the following pages an attempt is made to describe a definite scheme of analysis. The elements present are first determined in order to ascertain to which main group the compound belongs. The tests for particular radicles are then made, and so the field of investigation is considerably reduced. The melting-point of the substance, if a solid, or the boiling-point and density of the substance, if a liquid, serve to identify the compound, and its properties are compared with those given in the supplementary tables (paragraph **273** *et seq.*).

Before the analysis is commenced it is necessary to establish the purity of the compound. If it is found, or known, to be a mixture, its constituents must be separated before attempting identification. Methods of separating mixtures of organic compounds are outlined in paragraphs **359–364.**

251. Establishment of Purity.—The sharpness of melting-point or the constancy of boiling-point usually afford valuable confirmation of the purity of an organic substance. If on re-crystallisation a product is obtained with the same melting-point, its purity may in general be assumed. Methods of purifying crude organic compounds are given in detail in pages 1–8. The determination of boiling-point and of melting-point are described on pages 8–13.

DETECTION OF ELEMENTS

252. Carbon and Hydrogen.—It is usually unnecessary to test for the presence of these two elements, as evidence of the organic nature of a compound is afforded by the fact that on heating on porcelain the substance is inflammable and frequently chars. If

it contains four or more carbon atoms in the molecule it usually burns with a smoky flame and often leaves a carbon residue. Carbon and hydrogen may be positively identified by the following test.

Intimately mix a small quantity of the dry substance with about twenty times its weight of anhydrous, powdered copper oxide and heat strongly in a dry test tube. Pass the evolved gases into lime water to test for carbon dioxide, showing the presence of carbon in the original substance. Hydrogen, if present, is simultaneously converted into water, which will condense as beads of moisture in the cool, upper part of the tube. The presence of water may be confirmed by allowing the moisture to react with some white anhydrous copper sulphate placed in the upper part of the tube.

253. Nitrogen, Halogens and Sulphur.—*Lassaigne's Test.*—If an organic substance is heated with metallic sodium the nitrogen present will be converted into sodium cyanide, the halogens into sodium halides and the sulphur into sodium sulphide.

Introduce into a clean ignition tube a pellet of sodium the size of a small pea and cover it with about 2–3 mg. of the substance. Heat the mixture in a Bunsen flame, at first gently and finally to dull redness. Then plunge the tube whilst still hot into about 15 c.c. of distilled water contained in a small porcelain dish; the glass will be shattered and any unchanged sodium destroyed. Boil for one minute and filter. Divide the filtrate into three parts.

Test for Nitrogen.—To one part of the filtrate from the sodium fusion add a little saturated ferrous sulphate solution and 1 drop of a solution of ferric chloride. Boil for one minute, cool under the tap and add an excess of concentrated hydrochloric acid. The formation of a bluish-green solution followed by the gradual precipitation of prussian blue indicates the presence of nitrogen in the original compound.

Not balanced

$$\longrightarrow 6NaCN + Fe(OH)_2 \longrightarrow Na_4Fe(CN)_6 + 2NaOH$$
$$3Na_4Fe(CN)_6 + 4FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$$

Test for the Halogens.—To another part of the filtrate from the sodium fusion add an excess of pure nitric acid, boil and add silver nitrate solution. A precipitate of silver chloride, bromide or iodide indicates the presence of halogen in the original compound. Silver chloride, white in colour, is easily soluble in ammonium hydroxide; silver bromide, pale yellow, is soluble only with difficulty; silver iodide, yellow, is insoluble in ammonium hydroxide.

Test for Sulphur.—To another part of the filtrate from the sodium fusion add a freshly prepared solution of sodium nitro-

prusside. The formation of a violet coloration indicates the presence of sulphur in the original compound.

254. Halogen.—*Beilstein's Test.*—Heat a piece of copper wire in the Bunsen flame until it no longer imparts a green colour to the flame. Allow the oxidised wire to cool somewhat and then dip it into the organic compound. Re-heat in the flame. The appearance of a bluish-green flame on strongly heating indicates the presence of halogen in the compound.

255. Nitrogen.—*Mulliken and Gabriel's Test.*—In the case of compounds that are explosive or very volatile, or of which only a very small quantity can be spared for the experiment, it is advisable to test for nitrogen by the following modification of Lassaigne's test (**253**). Intimately mix about 1 cgm. of the substance with ten times its weight of pure naphthalene and compress the mixture into three or four pellets. Decompose these pellets in an ignition tube with sodium in the usual manner. Add to the concentrated, filtered, alkaline solution obtained from the fusion, about five drops of slightly oxidised, saturated ferrous sulphate solution and boil for several minutes. Add a slight excess of hydrochloric acid and leave for half-an-hour. If the solution is still apparently free from precipitate or green colour, filter through a very small wetted filter paper, wash the paper thoroughly first with hot dilute hydrochloric acid and then with water. After drying, a scanty blue coloration will be seen on the paper if the substance taken contained as much as 0·0001 gm. of nitrogen.

It must be remembered that the sodium fusion test cannot be relied upon for the detection of nitrogen in the $-N=N-$ group of diazonium salts, as these substances lose their nitrogen at very low temperatures.

256. Sulphur.—An alternative method for the detection of sulphur in an organic compound (compare paragraph **253**) consists in fusing the substance with alkali and an oxidising agent, whereby a sulphate is produced. Heat together in a small nickel crucible, at first gently and then to fusion, an intimate mixture of 0·2 gm. of the substance, 2 gm. of pure sodium carbonate and 1 gm. of sodium peroxide. Cool, extract with water, acidify with hydrochloric acid and test for sulphate by means of barium chloride solution. This method may be used for the quantitative estimation of sulphur. See paragraph **411**.

257. Phosphorus, Arsenic and Antimony.—Fuse together in a

nickel crucible a mixture of the compound, sodium carbonate and sodium peroxide, as described in the previous paragraph. Extract the cold melt with water and filter. Divide the filtrate into two parts.

To test for arsenic and antimony, acidify one part of the filtrate with hydrochloric acid and pass sulphuretted hydrogen through the boiling solution. Arsenic and antimony, if present, are precipitated as sulphides.

To test for phosphorus, add to another part of the filtrate an excess of concentrated nitric acid and test for phosphate by adding the solution to an excess of ammonium molybdate solution and warm. As a yellow precipitate is also formed by arsenic, the latter element, if present, must be first removed from the solution by precipitation as sulphide.

258. Mercury.—Mix a small quantity of the organic compound with soda-lime and heat strongly in a test tube. The formation of a mirror, and afterwards of globules of mercury, in the cold part of the tube indicates the presence of this metal.

259. Metals.—The presence of metals other than arsenic, antimony and mercury is shown by the formation of an ash on igniting an organic compound on platinum or porcelain. The nature of the metal is determined by dissolving the ash in dilute hydrochloric acid and examining the solution in the usual manner.

260. Determination of Density.—In the case of organic liquids the determination of density is of the greatest help in identification. The following method allows the density to be measured in three minutes and gives results sufficiently accurate for this purpose. A small pipette, delivering about 2 c.c., and a stoppered weighing bottle should be reserved for this determination. The actual capacity of the pipette is previously determined by weighing the mass of water that it delivers under normal conditions. This determination need be made only once and the same pipette kept for subsequent density measurements. The determination of the density of the organic liquid is then made in the following manner. Carefully fill the pipette to the mark with the organic liquid and allow it to drain out into the weighed measuring bottle. Replace the stopper and reweigh the bottle. Then if w_1 is the weight of the water delivered by the pipette and w_2 the weight of the organic liquid delivered, the approximate density Δ of the liquid is given by the formula :

$$\Delta = \frac{w_2}{w_1}$$

More accurate methods of determining the density of liquids and solids are given on pages 13–17.

THE QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS. GENERAL SCHEME

265. Before commencing the analysis of an organic substance the homogeneity of the compound should be established, unless it is known to be a single substance. If the substance is a liquid it should be distilled and the constancy of its boiling-point shown. If it is a solid, the melting-point should be taken and compared with the melting-point of a recrystallised specimen. The purity of the compound having been established, the tests given in the table below are then carried out.

Mixtures of organic compounds must first be separated before attempting the identification of the constituents. Methods of separating organic mixtures are outlined in paragraphs **359–365** and in the Analysis Tables XIII., XIV. and XV.

GENERAL TABLE I

I. If the substance is a solid: **Determine M.P.** (see page 8).

II. If the substance is a liquid: **Determine B.P.** (see page 11).
and Δ (see page 130).

III. **Ignite a small quantity of the substance on platinum, porcelain, or a nickel spoon.** If it burns with a smoky flame it indicates the probable existence of four or more carbon atoms in the molecule. A residual ash indicates the presence of a metal other than Hg, As and Sb. Dissolve the ash in dilute HCl and determine the nature of the metal in the usual manner.

If the compound burns with vigour and a brilliant flame it suggests the presence of a nitro-compound.

IV. **Determine the elements present** (see pages 127–130), and then turn to the appropriate table of analysis as shown below:

Elements present.	Analysis Table.	Page.
C.H.[O]	II. Preliminary tests	132
	III. Generic tests to determine nature of compound	132
	IV. Special table. The analysis of esters	142
C.H.[O]. Halogen	V. General table	183
C.H.[O].S.	VI. General table	193
C.H.[O].N.	VII. Preliminary tests	198
	VIII. Generic tests	199
	IX. Special table. Analysis of compounds, evolving NH_3 on Hydrolysis	216
C.H.[O].N. Halogen	X. General table	249
C.H.[O].N.S.[Halogen]	XI. General table	256
C.H.[O].S. Halogen	XII. General table	262

266. Analysis of Compounds containing C.H.[O] only. Preliminary Tests.

TABLE II

Odour.

Pleasant ethereal odour : esters, etc.

Pungent odour : simple acids of low molecular weight, quinones, acid anhydrides, etc.

Colour.

If well defined : quinones, diketones, aromatic ketones, etc.

Solubility in water and action of litmus.

Relatively insoluble : esters, ethers, hydrocarbons, higher alcohols, aldehydes, ketones, quinones, etc.

Acid in reaction : acids, some esters, acid anhydrides.

Faintly acid : phenols, polyhydric phenols.

NOTE.—Phenols and polyhydric phenols do not liberate CO_2 from $NaHCO_3$.

Heat with conc. H_2SO_4.

Chars with burnt sugar smell : carbohydrates, tartrates, citrates, etc.

Chars : polyhydric phenols, phenolic acids, aldehydes, ketones, etc.

CO, CO_2, evolved : oxalate.

CO evolved : formate, lactate, etc.

Purple or red colour in cold : glucosides.

Treat with NaOH solution : then heat.

Soluble in cold NaOH although insoluble in water : acids, phenols, enols, etc.

Gradually dissolve on heating : esters, acid anhydrides, etc.

Turns yellow or brown : aldehydes, some phenols and carbohydrates, etc.

Soluble with intense colour : phthaleins, pyronines, derivatives of alizarine, rosolic acid, etc.

Treat with alkaline $KMnO_4$ solution.

Decolorised : unsaturated compounds and easily oxidisable compounds.

Treat with Br dissolved in water, and warm.

Decolorised : unsaturated compounds; some aldehydes and ketones. Readily brominated compounds, such as phenol.

Treat with Br dissolved in CCl_4, and warm.

Decolorisation : unsaturated compounds.

Decolorisation and evolution of HBr : substances which are readily brominated.

267. Compounds containing C.H.[O] only. Generic Tests to determine Nature of Compound.

TABLE III

A. Add a small quantity of the substance to 5 c.c. of decolorised magenta solution. Leave for two minutes, shaking if insoluble. Do not heat.

If a pink, red or blue colour is obtained the substance is an aldehyde. If solid, identify by tables on page 135 ; if liquid, by tables on page 135. If the substance is a solid and neutral, and does not answer to this test, apply test **B** below ; if a liquid, proceed to test by **C** below.

B. To a small quantity of the substance in a test tube add 0·5 c.c. of water and 2 drops of chloroform containing a little α-naphthol. Carefully add 1 c.c. of pure sulphuric acid so that it forms a layer below the aqueous solution.

The formation of a red ring at the junction of the layers indicates the presence of a carbohydrate. (The Molisch Reaction.) This test is not valid in the presence of glucosides. If a positive result is obtained, identify by the tables on page 138; if negative, proceed to test by **C** below.

C. Dissolve about 0·2 gm. of the substance in water or dilute alcohol, add a little phenolphthalein and then N/10 NaOH drop by drop until an end-point is reached.

If more than about 0·5 c.c. of alkali is required and the end-point is sharp, the compound is probably an acid. Acid anhydrides and esters usually contain free acid, and many of them are slowly hydrolysed with dilute alkali. If these are believed to be present reflux some of the substance with 10 per cent. alkali for at least half an hour. Distil off volatile alcohols set free from esters and examine the residual solution for the acid and non-volatile alcohols present as described on page 142. If the acid is of the aromatic series it is usually readily obtained on acidifying with conc. HCl and cooling.

Identify the acid, if liquid, by tables on page 149, and if solid by the tables on page 143. The properties of solid esters are given in the tables on page 152; of liquid esters on page 154; of alcohols on page 173; and of phenols on page 161.

If the compound does not belong to class **C**, proceed with test **D** below.

D. To a little of the substance dissolved in water or dilute alcohol add 2 drops of a dilute solution of ferric chloride.

The formation of a blue, green or violet coloration indicates the presence of phenols, phenolic compounds or a keto-enolic ester. A reddish coloration or precipitate indicates a simple carboxylic acid; an intense yellow the presence of a hydroxy-acid.

Tables for the identification of phenols are given on page 161; of acids on pages 143–150; and of esters on page 152. If this test gives a negative result proceed to test by **E** below. [**A few solid phenolic compounds do not give a colour reaction with ferric chloride, but are soluble in 10 per cent. caustic soda. If the substance under examination is relatively insoluble in water but soluble in alkali, and does not belong to the acid class, it should be sought amongst the phenols.**]

E. Dissolve a small quantity of the substance in water or dilute alcohol and shake gently with a few drops of phenylhydrazine dissolved in dilute acetic acid. Warm, if necessary, by immersing the tube in boiling water for five minutes. Cool.

The formation of an opaque solution, or of a precipitated phenylhydrazone, indicates the presence of a ketone, which, if solid, should be identified by the tables on page 168, and if liquid, by the tables on page 171. If any doubt exists as to whether the substance is a ketone one or more of the supplementary generic tests given on page 168 should be applied. If the above test gives a negative result proceed with test **F** below.

F. Add a few drops of the substance, if liquid, to a piece of clean sodium contained in a small dry tube. If solid, first dissolve the substance in dry benzene and then add to the sodium. Warm to about 80° C. if necessary.

The rapid disengagement of gas, and a change in appearance of the metal, indicates the presence of a hydroxylic compound, although it must be remembered that moisture present in an inert organic liquid will react in the same way. If the substance is reasonably soluble in water (*i.e.*, more than 5 per cent.), and has not

answered to previous generic tests, it necessarily belongs to this group and not to G below. Identify the alcohol, if present, by the tables on page 173.

G. All substances that have failed to answer to generic tests A—F, fall in this class of unreactive substances.

If solid, identify by tests on page 177; if liquid, by tests on page 179.

THE IDENTIFICATION OF ALDEHYDES CONTAINING C.H.O ONLY

268. General Remarks.—Nearly all aldehydes have characteristic odours and exhibit a great tendency to polymerise in the presence of acids and alkalies. Many of them resinify or darken in colour on warming with NaOH solution, and dissolve in H_2SO_4 with decomposition. They answer to generic test A, given in the previous paragraph, and in addition readily form phenylhydrazones, oximes, semi-carbazones and $NaHSO_3$-addition compounds, although in a few cases the derivatives are too soluble to crystallise out readily. They usually reduce alkaline $KMnO_4$ and ammoniacal $AgNO_3$.

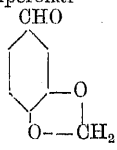
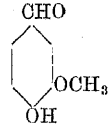
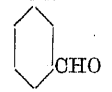
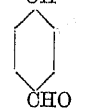
269. Formation of Phenylhydrazones.—Phenylhydrazones can be prepared either by method E, paragraph **267**, or in the following way. Dissolve equal quantities of the substance, phenylhydrazine hydrochloride and sodium acetate, in 15–20 parts of water and, if necessary, add just sufficient pure alcohol to effect solution. Warm on the water bath for thirty minutes or until, on cooling, the hydrazone crystallises out. Recrystallise from dilute alcohol. See preparation 35, page 58.

270. Formation of Oximes.—Oximes may be prepared by the method described in preparation 31, page 55.

271. Formation of Semi-carbazones.—Mix together a small quantity of the substance, semi-carbazide hydrochloride and sodium acetate, with water. If necessary, add sufficient pure alcohol to effect solution. Shake and warm on the water bath until the semi-carbazone crystallises on cooling. Recrystallise from dilute alcohol. See preparation 34, page 58.

272. Reduction of $AgNO_3$. Tollen's Reaction.—Shake together for five minutes, *without warming*, a little of the substance with equal volumes of 10 per cent. ammoniacal $AgNO_3$ and 10 per cent. NaOH, prepared as described in paragraph **514**. A reducing agent, such as an aldehyde, yields either a silver mirror or a black precipitate of reduced silver. A few aromatic oxy-aldehydes, such as vanillin and salicylaldehyde, do not give this reaction.

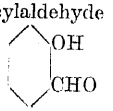
273. Properties of Solid Aldehydes containing C.H.O only.

M.Pt. °C.	Name.	Characteristics.
37	Piperonal 	Needles. B.P. 263°. Odour of heliotrope. i.s. cold water ; e.s. alcohol, ether. Oxime, M.P. 110°. Phenylhydrazone, M.P. 100° Nitrated with pure HNO_3 gives nitro-compound in yellow needles, M.P. 95°.
80	Vanillin 	Needles. Odour of vanilla. s.s. water ; e.s. alcohol, ether, $CHCl_3$. Blue colour with $FeCl_3$. Br-water → bromo-compound, M.P. 160°. Oxime, M.P. 117°. Phenylhydrazone, M.P. 105°.
104	*m*-oxybenzaldehyde 	Needles. s.s. water. $FeCl_3$ → violet colour. PbA_2 → white precipitate.
115	*p*-oxybenzaldehyde 	Sublimes. s.s. water ; e.s. alcohol, ether. $FeCl_3$ → faint violet colour. Oxime, M.P. 72°. Phenylhydrazone, M.P. 176°.
115 Sublimes.	Metaldehyde $(CH_3.CHO)_3$	Crystalline. i.s. water ; d.s. alcohol, ether. Distilled with dil. H_2SO_4 → acetaldehyde.
175	Helicine $C_{13}H_{16}O_7 + H_2O$	s.s. water ; e.s. alcohol ; i.s. ether. Optically active. Hydrolysed by dilute acids to salicyl-aldehyde and glucose. With Na amalgam gives salicin.

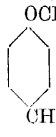
274. Properties of Liquid Aldehydes containing C.H.O only.

B.P. °C.	Δ	Name.	Characteristics.
21	0·806 (0°)	Acetaldehyde $CH_3.CHO$	Pungent ethereal odour. Miscible with water, alcohol, ether. Boil with excess of 10 per cent. NaOH for two minutes → opaque solution, yellow-brown colour, and powerful odour.
45·5	0·872 (15°)	Methylal $(CH_3O)_2 : CH_2$	Ethereal odour. e.s. water. Boil with dil. HCl → H.CHO (*q.v.*).

Properties of Liquid Aldehydes—*continued.*

B.P. °C.	Δ	Name.	Characteristics.
52·5	0·840	Acrolein $CH_2 : CH.CHO$	Excessively irritating odour. Lachrymatory. e.s. water, unsaturated. Polymerises to insol. solid readily. Mix one drop of solution with 5 drops of alcoholic gallic acid solution and 2 c.c. of water, and pour on to cold conc. H_2SO_4 in tube without mixing → orange layer at junction.
97	—	Formalin H.CHO. 40 per cent. solution.	Pungent odour. Distillation → residue of white paraformaldehyde in flask. Boil 3 drops with 1 c.c. of alcohol, 2 c.c. of water, 0·05 gm. β-naphthol and 5 drops of conc. HCl. Filter hot and wash with alcohol → methylene-*di*-β-naphthyl ether, $C_{10}H_7O.CH_2.OC_{10}H_7$, white needles. M.P. 190°. Add equal volumes of phenylhydrazone hydrochloride solution and dilute sodium nitroprusside solution to dilute formalin and excess NaOH → intense blue colour.
104	0·831 (20°)	Acetal $(C_2H_5O)_2 : CH.CH_3$	Agreeable odour. s.s. water. Dilute solution plus HCl → acetaldehyde (*q.v.*).
124	0·999 (15°)	Paraldehyde $(CH_3.CHO)_3$	M.P. 10°. Agreeable odour. 10 per cent. soluble in water. Heat with very little conc. H_2SO_4 → acetaldehyde (*q.v.*).
161	1·159 (20°)	Furfural $C_4H_3O.CHO$	Darkens in air. Peculiar odour. Phenylhydrazone, pale yellow, pearly lustre, M.P. 97°. Boil furfural with excess water and hold paper moistened with glacial acetic acid and aniline in vapour → bright red colour.
179	1·050 (15°)	Benzaldehyde $C_6H_5.CHO$	Odour of almonds. s.s. water. Phenylhydrazone, M.P. 156°. Oxidised with alkaline $KMnO_4$ → benzoic acid, M.P. 121°. Heat with strong KOH → potassium benzoate and benzyl alcohol, B.P. 205°.
196	1·173 (13°)	Salicylaldehyde 	Faint odour. s.s. water; e.s. alcohol, ether. $FeCl_3$ and aqueous solution → intense violet colour. Phenylhydrazone, M.P. 142°. Oxidation with alkaline $KMnO_4$ → salicylic acid, M.P. 155°.

Properties of Liquid Aldehydes—*continued.*

B.P. °C.	Δ	Name.	Characteristics.
206	0·854 (18°)	Citronellal $C_9H_{17}.CHO$	Strong odour of geraniums. Optically active. Semi-carbazone, M.P. 84°.
215–220 *d.*	1·050 (24°)	Cinnamic aldehyde $C_6H_5.CH{:}CH.CHO$	Odour of cinnamon. i.s. water. Unsaturated. Phenylhydrazone, M.P. 168°. Acid $KMnO_4$ → benzaldehyde (odour of almonds). Alkaline $KMnO_4$ → benzoic acid, M.P. 121°. Warmed with conc. KOH → cinnamic acid, M.P. 133°, and cinnamyl alcohol, M.P. 33°, B.P. 250°.
228	0·897 (15°)	Citral $C_9H_{15}.CHO$	Odour of lemons. Optically active. Semi-carbazone, M.P. 164°.
235	0·983	Cuminic aldehyde 	Characteristic odour. Phenylhydrazone, M.P. 127°, white in colour. Oxidation with alkaline $KMnO_4$ → terephthalic acid, which sublimes without melting above 300°, and is insoluble in water and in alcohol.
248	1·123	Anisic aldehyde 	Aromatic odour. i.s. water. Phenylhydrazone, M.P. 120° (white). Heated with alcoholic KOH → anisic acid, M.P. 184°, and anisic alcohol, M.P. 45°, B.P. 259°.

THE IDENTIFICATION OF CARBOHYDRATES CONTAINING C.H.O ONLY

275. General Remarks.—Carbohydrates are solids that seldom melt sharply, and are very difficult to crystallise from their syrupy solutions. They are optically active, and the determination of the degree of optical activity (see page 19), the formation of osazones (see page 59), and their action towards Fehling's solution (see paragraph **466**) afford valuable evidence of identification. They are distinguished from glucosides by the action of strong sulphuric acid, with which the glucosides give a red-purple colour in the cold, and with the carbohydrates turn brown and char on heating. The glucosides are tabulated in this book with phenolic compounds (see page 161).

The polysaccharides, such as starch and cellulose, are much less soluble than the mono- and di-saccharides. They do not reduce Fehling's solution nor form osazones. On hydrolysis with acids they form hexoses. They give characteristic colour reactions with iodine.

276. Properties of Carbohydrates containing C.H.O only, which are moderately soluble in water, forming clear solutions.

M.P. °C.	Specific Rotation.	Name.	Characteristics.
85–90	—	Dextrose $C_6H_{12}O_6+H_2O$	See Dextrose, anhydrous, M.P. 146°.
94–95	$[a]_D = -92{\cdot}5°$	Lævulose (Fructose) $C_6H_{12}O_6$	Hygroscopic needles from alcohol: $+\frac{1}{2}H_2O$ from water. v.s. in alcohol, water; moderately so in ether. Osazone readily formed, M.P. 204°. Reduces Fehling's solution.
118	$[a]_D = +104°$	Raffinose $C_{18}H_{32}O_{16}+5H_2O$	Needles, losing $5H_2O$ above 100°. e.s. in water; moderately in methyl alcohol; i.s. ethyl alcohol. Osazone only formed after heating for at least one hour. Does not reduce Fehling's solution.

Properties of Carbohydrates—*continued.*

M.P. °C.	Specific Rotation.	Name.	Characteristics.
132	$[a]_D = +14{\cdot}25°$	*d*-Mannose $C_6H_{12}O_6$	Prisms from alcohol. e.s. water; s.s. alcohol. Reduces Fehling's solution. Readily forms an almost colourless *phenylhydrazone*, M.P. 195–200°.
146	$[a]_D = +52{\cdot}8°$ in solution containing NH_4OH. See page 21.	Dextrose (Glucose) $C_6H_{12}O_6$	Needles from alcohol. From water $+1H_2O$, M.P. 85–90°. e.s. water, hot alcohol; i.s. ether. Yellow osazone separates after five to ten minutes, M.P. 204°. Reduces Fehling's solution.
160	$[a]_D = +104{\cdot}5°$	*l*-Arabinose $C_5H_{10}O_5$	Prisms. v.s. water; s.s. alcohol; i.s. ether. Yellow osazone, M.P. 160°, slowly formed. Reduces Fehling's solution.
160–170 *d.*	$[a]_D = +66{\cdot}5°$	Sucrose (Cane Sugar) $C_{12}H_{22}O_{11}$	Colourless crystals. e.s. water; s.s. alcohol. Osazone, M.P. 204, formed only after prolonged heating. Does not reduce Fehling's solution. Warmed with dilute HCl $\longrightarrow$ invert sugar (dextrose and lævulose), which reduces Fehling's solution and gives $[a]_D = -19{\cdot}8°$.
168	$[a]_D = +81{\cdot}0°$ exhibits muta-rotation.	*d*-Galactose $C_6H_{12}O_6$	Prisms. From water forms $+1H_2O$, M.P. 118–120°. e.s. water; s.s. alcohol. Orange-yellow osazone, slowly formed, M.P. 196°. Reduces Fehling's solution.
200 *d.*	$[a]_D = +52{\cdot}5°$	Lactose (Milk Sugar) $C_{12}H_{22}O_{11}+H_2O$	Large crystals, lose H_2O at 130°, turn yellow at 160°. s. water; i.s. alcohol, ether. Osazone separates only on cooling hot solution after prolonged heating, M.P. 200° *d.* Reduces Fehling's solution.
—	$[a]_D = +137{\cdot}8°$	Maltose (Malt Sugar) $C_{12}H_{22}O_{11}+H_2O$	Decomposes on heating. v.s. water; s.s. alcohol. Osazone separates only on cooling after prolonged heating, M.P. 206°. Reduces Fehling's solution.

277. Properties of Carbohydrates containing C.H.O only, which are Insoluble in water or give opalescent solutions.

M.P. °C.	Name.	Characteristics.
178 *d.*	Inuline $C_{36}H_{62}O_{31}$	Tasteless, white powder. Soluble in hot water, from which it does not separate on cooling; i.s. alcohol. $[a]_D = -39{\cdot}5°$. Slowly forms osazone. No colour with I_2. Does not reduce Fehling's solution. Boiled with dilute HCl ⟶ principally lævulose.
240 *d.*	Glycogen $C_6H_{10}O_5$.	Intensely opalescent solution. i.s. alcohol. Does not form osazone or reduce Fehling's solution. $[a]_D = +198°$.
—	Dextrine	A mixture. Soluble in hot water ⟶ gum. Brown colour with iodine. No osazone. Usually reduces Fehling's solution. Boiled with dilute HCl is hydrolysed, and then reduces Fehling's solution readily, due to formation of dextrose.
—	Starch $(C_6H_{10}O_5)_n$.	i.s. cold water, alcohol, ether. Soluble in hot water ⟶ thick solution. Blue colour with iodine. Hydrolysed with dilute acid ⟶ dextrine ⟶ glucose.
—	Cellulose $(C_6H_{10}O_5)_n$.	Insoluble in all ordinary solvents. No action with iodine. Soluble in cuprammonium hydroxide (prepared by dissolving freshly precipitated $Cu(OH)_2$ in strong ammonia). Is reprecipitated from this solution by acids.

THE IDENTIFICATION OF ACIDS, ACID ANHYDRIDES AND ESTERS CONTAINING C.H.O ONLY

278. General Remarks.—Substances belonging to these classes will have been indicated by the fact that they are nearly all acid in reaction. Acids on titration with NaOH in aqueous or alcoholic solution, using phenolphthalein as an indicator, give a sharp end-point. Most anhydrides and many esters are slowly hydrolysed and thus react acid. The majority of esters have agreeable and highly characteristic odours.

In order to prove conclusively that a compound is an anhydride or an ester, it should be heated with a known quantity of standard alkali and the amount of the latter used in saponification determined in the following manner. Carefully weigh about 0·3 gm. of the substance in a stout test tube. Add 10 c.c. of alcoholic potash, about normal strength. Tightly stopper the tube, securing the cork with copper wire. As a blank experiment, place 10 c.c. of the alcoholic potash in a second tube. Immerse the two tubes in water at 80°–90° C. for half an hour and then wash the contents of each into separate beakers. Titrate each with standard acid, using phenolphthalein as an indicator. From the difference in the two titrations the amount of alkali used to effect saponification can be calculated, and hence the saponification equivalent of the ester or anhydride (see paragraph **442**).

If sufficient material is available, a larger quantity, say, 2 gm., should be refluxed with 50 c.c. of 10 per cent. aqueous alkali and both the alcohol (or phenol) and acid isolated and identified. The saponification must be continued until the appearance and odour of the mixture suggest that the reaction is complete. Two drops of phenolphthalein are then added and normal sulphuric acid run in until exactly neutral, and about 20–30 c.c. rapidly distilled off through a water condenser. The great majority of the alcohols and phenols will be removed in this way. The following table indicates the procedure to be adopted.

279. The Qualitative Examination of Esters. TABLE IV

Reflux about 2 gm. of the ester with 50 c.c. of 10 per cent. NaOH solution until saponification is complete. Neutralise with dilute H_2SO_4, using phenolphthalein as an indicator. Distil the whole until about 25 c.c. of distillate have been collected.

Residual Liquid.—Filter if necessary. Add excess of concentrated HCl. Cool and filter.

***Precipitate.**—Wash with a little cold water. A residual precipitate shows the presence of an **insoluble acid** such as benzoic or salicylic. Identify in the usual manner.

* NaCl may be precipitated at this stage by the concentration of the HCl used.

Filtrate may contain soluble acids and glycerol. Distil until one half of its volume has been collected.

Distillate may contain **steam-volatile soluble acids** such as acetic. Exactly neutralise with NaOH, evaporate and examine residual sodium salt.

Residual Liquid may contain **soluble, non-volatile acids** such as tartaric acid, also **glycerol.** Evaporate just to dryness, extract with ether. Examine the residue obtained on distilling off the ether.

Distillate will contain the steam-volatile alcohols and phenols.

If the distillate is turbid the presence of partially soluble alcohols is indicated, such as **phenol** (characteristic odour), **allyl alcohol** (pungent odour), iso-**butyl** and **amyl alcohols** (disagreeable odours) and **benzyl alcohol** (faintly aromatic odour).

If the distillate is homogeneous and the odour mildly alcoholic, test for :

Methyl alcohol by plunging in a red-hot Cu wire and testing the solution for formaldehyde, as described on page 174.

Ethyl alcohol by the iodoform reaction on warming to 60° C. (see page 175).

iso-**Propyl alcohol** by the iodoform reaction in the cold (see page 175).

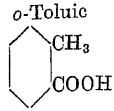
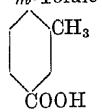
Other alcohols by extraction with ether, evaporation, and examination of the B.P. and Δ of the residual alcohol.

280. Acids may be identified by the preparation of esters. This is best done by dissolving the acid in an excess of absolute alcohol and passing in dry hydrochloric acid gas (see preparation 45, page 73). The resultant ester can be separated either by pouring into water or by simple distillation. **α-Hydroxy-acids** give with aqueous ferric chloride an intensely yellow solution, simple carboxylic acids give reddish colorations or precipitates, and **phenolic acids** give violet or bluish colours with the same reagent. If an aliphatic α-hydroxy acid is suspected, the colour obtained with ferric chloride should be compared with that produced by tartaric acid under similar conditions. The neutralisation equivalent of the acid can also be determined as described in paragraph **442**.

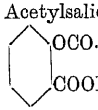
281. Properties of Solid Acids containing C.H.O only.

M.P. °C.	Name.	Characteristics.	Methyl ester, B.P. °C.	Ethyl ester, B.P. °C.
16 17	Acetic	See liquid acids (paragraph 282).	—	
18	Lactic $CH_3.CHOH.COOH$	Usually a syrup. B.P. 119° at 12 mm. Miscible with water, alcohol and ether. Gives hydroxy-acid test with $FeCl_3$. Reduces $KMnO_4$ with effervescence, giving pyruvic acid.	144	154
48	Hydrocinnamic $C_6H_5.CH_2.CH_2.COOH$	B.P. 280°. s.s. water. Ba salt only s.s. Oxidised by CrO_3 to benzoic acid, M.P. 121.	236	247
62·5	Palmitic $CH_3.(CH_2)_{14}.COOH$	Greasy to touch. i.s. water, s. alcohol. Acid in reaction in alcoholic solution. Soapy solution in alkalies.	M.P. 28	M.P. 24
69·5	Stearic $CH_3(CH_2)_{16}COOH$	Compare palmitic acid. i.s. water, s. alcohol, e.s. ether. Ca and Ba salts precipitated.	M.P. 38	M.P. 24
76·5	Phenylacetic $C_6H_5.CH_2.COOH$	B.P. 265°. v.s. hot water, alcohol, ether. Oxidised by acid $KMnO_4$ to $C_6H_5.CHO$, by alkaline $KMnO_4$ to $C_6H_5.COOH$, M.P. 121°.	220	227

Properties of Solid Acids—*continued.*

M.P. °C.	Name.	Characteristics.	Methyl ester, B.P. °C.	Ethyl ester, B.P. °C.
78	Glycollic $CH_2OH.COOH$	Deliquescent. s. in ether. Ba and Cu salts precipitated. Ag salt soluble. With HNO_3 gives oxalic acid. Gives α-hydroxy-acid test with $FeCl_3$.	151	160
98–99	Oxalic $COOH$ | $COOH + 2H_2O$	Loses water at 98°, then sublimes at 150–160°. e.s. water, alcohol; s.s. ether. Heated with conc. H_2SO_4 gives CO, CO_2, without charring. Ca salt insoluble in acetic acid. Oxidised to CO_2 at 60° with acid $KMnO_4$.	M.P. 51 163	— 186
100	Malic $CH_2.COOH$ | $CHOH.COOH$	Optically active. v.s. water, alcohol, ether. Gives α-hydroxy-acid test with $FeCl_3$. Pb, Ag, salts insoluble. Ba salt soluble. At 180–200° gives fumaric acid and maleic anhydride. Heat 0·05 gm. in dish or water bath with 1 c.c. of conc. H_2SO_4 containing trace of β-naphthol. Intense yellow colour. Compare citric acid and tartaric acid.	122 at 12 mm.	129 at 12 mm.
102	*o*-Toluic 	B.P. 259°. m.s. hot water; v.s. alcohol. Oxidised by alkaline $KMnO_4$ to phthalic acid, M.P. 195°.	207	221
110	*m*-Toluic 	B.P. 263°. s.s. water; e.s. alcohol, ether. Oxidised by alkaline $KMnO_4$ to *iso*-phthalic acid, M.P. above 300°.	214	227
121	Benzoic $C_6H_5.COOH$	B.P. 249°. Needles; m.s. hot water; e.s. alcohol, ether. Nitrated with H_2SO_4 and fuming HNO_3 to *m*-nitrobenzoic acid, M.P. 140°. Buff-coloured precipitate with $FeCl_3$, soluble in ammonia. Ag salt soluble in hot water.	198	213

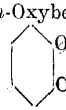
Properties of Solid Acids—*continued.*

M.P. °C.	Name.	Characteristics.	Methyl ester, B.P. °C.	Ethyl ester, B.P. °C.
130	Maleic CH.COOH ‖ CH·COOH	Monoclinic prisms. e.s. water. Unsaturated. With hot Br-water gives di-brom-succinic acid, M.P. 160°. Does not react readily with Br in CCl_4. Heated to 120° in vacuo gives anhydride, M.P. 56°. Strongly heated gives fumaric acid, sublimes 200°. Ba, Pb, salts insoluble. Ca salt soluble.	205	225
132	Malonic $CH_2(COOH)_2$	v.s. water; s. ether. Heated to 200° loses CO_2, and gives acetic acid. Br-water gives tribromacetic acid, M.P. 135°. Ca, Ba, Ag salts insoluble.	181	198
133	Cinnamic $C_6H_5.CH : CH.COOH$	B.P. 300°. Faint odour. s.s. water: s. alcohol, v.s. ether. Unsaturated. Oxidised by acid $KMnO_4$ to benzaldehyde, by alkaline $KMnO_4$ to benzoic acid. With hot Br-water gives dibrom-derivative, M.P. 195°. Nitrated with fuming HNO_3 and product recrystallised from alcohol and washed with ether gives *p*-nitro-acid, M.P. 286°.	263	271
135	Acetylsalicylic 	"Aspirine." s.s. water. No colour with $FeCl_3$. Boiled with NaOH gives salicylic acid, M.P. 158°.	—	272
150	Benzilic $(C_6H_5)_2.C(OH).COOH$	Needles. e.s. hot water. Soluble in conc. H_2SO_4 with intense red colour. Gives α-hydroxy-acid test with $FeCl_3$. Oxidised by CrO_3 to benzophenone, M.P. 48°.	M.P. 74	M.P. 34
153	Citric $CH_2.COOH$ | $C(OH).COOH$ | $CH_2.COOH$	Prisms+H_2O. v.s. water, alcohol: s.s. ether. Gives α-hydroxy-acid test with $FeCl_3$. Hot conc. H_2SO_4 gives CO, CO_2, SO_2, with slight charring. Ca salt precipitated on boiling. The colour reaction given under malic acid (M.P. 100°) gives pale green.	M.P. 79	294 d.

Properties of Solid Acids—*continued.*

M.P. °C.	Name.	Characteristics.	Methyl ester, B.P. °C.	Ethyl ester, B.P. °C.
158	Salicylic 	Needles. s.s. hot water: v.s. alcohol, ether. Aqueous solution gives purple colour with $FeCl_3$. Nitrated with HNO_3 in 5 parts water for five minutes at 100°, and recrystallised from water, gives 5-nitro-acid, M.P. 226°. Esters have odour of oil of wintergreen. Br-water gives white precipitate.	224	231
160	α-Naphthoic $C_{10}H_7.COOH$	Needles. s.s. hot water; s. alcohol. Heated with soda-lime gives naphthalene. Ca salt precipitated.	—	309
169	*d*-Tartaric $\begin{matrix}CHOH.COOH\\ \vert\\ CHOH.COOH\end{matrix}$	Optically active $[\alpha]_D^{20} = +12°$. v.s. water, alcohol; s.s. ether. Ca salt precipitated in neutral solution. Chars with hot conc. $H_2SO_4 \rightarrow CO, CO_2, SO_2$. Gives α-hydroxy-acid test with $FeCl_3$. To aqueous solution add 1 drop of $FeSO_4$, 3 drops of H_2O_2 and excess of NaOH, gives deep violet colour. (Distinction citric, malic, succinic and oxalic acids.) The colour reaction described under malic acid (M.P., 100°), yields intense green colour. Reduces ammoniacal $AgNO_3$.	M.P. 48 280	280
176	*p*-Toluic 	B.P. 275°. v.s. hot water, alcohol, ether. Oxidised by alkaline $KMnO_4$ to terephthalic acid. Methyl-ester powerful and agreeable odour.	M.P. 32	228
181	*d*-Camphoric $C_8H_{14}(COOH)_2$	$[\alpha]_D = +47{\cdot}35$ (alcohol). s.s. water; e.s. alcohol; i.s. CS_2. Heated with conc. H_2SO_4 gives CO. Ba salt soluble. Pb salt precipitated.	265	285
183	β-Naphthoic $C_{10}H_7.COOH$	Silky needles. v.s.s. hot water; e.s. alcohol, ether. Ba and Ca salts precipitated. Yields naphthalene on heating with soda-lime.	M.P. 77 290	308

Properties of Solid Acids—*continued.*

M.P. °C.	Name.	Characteristics.	Methyl ester, B.P. °C.	Ethyl ester, B.P. °C.
184 d.	Phthalic 	Rhombic crystals. On melting gives anhydride which sublimes and melts about 128°. e.s. hot water, alcohol; i.s. chloroform. Heat with a little resorcinol and 1 drop $CHCl_3$ at about 160–180° for three minutes. Cool and add 2 c.c. of dilute NaOH and pour into water. Intense yellow-green fluorescence (fluorescein). Boiled with 4 parts of aniline for fifteen minutes gives phthalanil, which after crystallisation from alcohol gives M.P. 204°.	282	298
185	Succinic $CH_2.COOH$ | $CH_2.COOH$	Prisms, B.P. 235°, giving anhydride. e.s. water, alcohol; s.s. ether; i.s. $CHCl_3$. Gives yellowish coloration with $FeCl_3$, and reddish precipitate insoluble in acetic acid. Heated with 4 parts of *p*-toluidine at 200–220° for thirty minutes, or with 4 parts of aniline at 180–190° gives *p*-toluidide, M.P. 255°, and anilide, M.P. 226°.	M.P. 19 B.P. 195 Sol. in cold water.	216
189	Oxalic Acid Anhydrous COOH | COOH	Octahedra. *See* Oxalic acid, $(COOH)_2 . 2H_2O$ (M.P. 98°).		
Sublimes 200	Fumaric CH.COOH | CH.COOH	Melts in sealed capillary at 290°. s.s. water. Unsaturated. Heated with Br-water gives a di-brom-succinic acid, which decomposes at 200–220°. Ba salt precipitated.	M.P. 102 192	218
200	*m*-Oxybenzoic 	s.s. water. No colour with $FeCl_3$. Boiled with conc. H_2SO_4, gives orange-red solution. Heated with soda-lime gives phenol.	M.P. 70 230	M.P. 72 295

Properties of Solid Acids—*continued.*

M.P. °C.	Name.	Characteristics.	Methyl ester, B.P. °C.	Ethyl ester, B.P. °C.
200–210 d.	Tannic $C_{14}H_{10}O_9$	Pale-coloured powder. e.s. water; s.s. alcohol; i.s. ether. Aqueous solution + $FeCl_3$, gives deep blue colour. Alkaline solutions absorb oxygen and turn brown. Coagulates solution of gelatine. Reduces $AgNO_3$ on boiling.	—	—
205	Racemic CHOH.COOH | CHOH.COOH	+ H_2O, crystals effloresce in air. e.s. water; s. alcohol. Gives α-hydroxy-acid test with $FeCl_3$. Ba and Ag salts insoluble. Precipitates Ca salt from $CaSO_4$ soln., this precipitate is sol. in HCl, and reprecipitated by NH_4OH. (Difference from tartaric acid.)	M.P. 85 282	157 (11·5 mm.)
210	*p*-Oxybenzoic OH COOH	Prisms + H_2O. s.s. water. Yellow, amorphous precipitate with $FeCl_3$. Heated with soda-lime, or alone, gives phenol.	M.P. 131	M.P. 116
220–230 d.	Gallic OH OH HOOC OH	Silky needles + $1H_2O$. e.s. hot water. Alkaline solutions turn brown in air. Does not coagulate gelatine (cf. Tannic acid).	M.P. 192 d.	M.P. 141 anhydrous. M.P. 90 Hydrate
+ 300	*iso*-Phthalic COOH COOH	Fine needles. Sublimes. s.s. hot water; s. alcohol. Ba salt soluble. Ag salt precipitated, swells on heating.	M.P. 64	302
Sublimes + 300	Terephthalic COOH COOH	Amorphous powder. i.s. water, alcohol, ether. Ba, Ag, Ca salts precipitated.	M.P. 140	302 M.P. 44

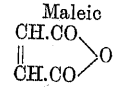
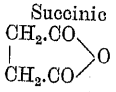
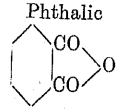
282. Properties of Liquid Acids containing C.H.O only.

B.P. °C.	Δ	Name.	Characteristics.	Methyl ester, B.P. °C.	Ethyl ester, B.P. °C.
101	1·245 (0°)	Formic H.COOH	Sharp odour. Miscible with water. Heated with conc. H_2SO_4 gives CO without charring. Decolourises acid $KMnO_4$. Warm to 40° with excess of HgO: filtrate on boiling gives a grey precipitate of Hg. Red colour with $FeCl_3$, destroyed by HCl. Reduces ammoniacal $AgNO_3$.	32	54
118	1·051 (20°)	Acetic CH_3.COOH	M.P. 16·7°. Sharp odour. Miscible with water. Is not a reducing agent. Red colour with $FeCl_3$, destroyed by HCl. Anilide, M.P. 113°. *p*-toluidide, M.P. 146°.	57	77
140	0·996 (19°)	Propionic C_2H_5.COOH	Odour like acetic acid. Miscible with water. Anilide, M.P. 105°. *p*-toluidide, M.P. 124°.	79	98
140	1·062 (16°)	Acrylic CH_2 : CH.COOH	Sharp odour. Miscible with water. Unsaturated, reduces alkaline $KMnO_4$. With Br gives $\alpha\beta$-dibrom-propionic acid (soluble in water, M.P. 64°). Alkali fusion gives formic and acetic acids.	85	101
155	0·949 (20°)	Isobutyric $(CH_3)_2$: CH.COOH	Odour of rancid butter. m.s. water. Oxidised by alkaline $KMnO_4$ to acetonic acid $(CH_3)_2$.COH.COOH, M.P. 79°. Anilide, M.P. 102°. *p*-toluidide M.P. 104°.	92	110

Properties of Liquid Acids—*continued.*

B.P. °C.	-Δ	Name.	Characteristics.	Methyl ester, B.P. °C.	Ethyl ester, B.P. °C.
162	0·960 (19°)	*n*-Butyric $C_3H_7.COOH$	Odour of rancid butter. Miscible with water, alcohol, ether. Saturated cold solution of Ca salt gives precipitate on heating (difference from iso-acid). Anilide, M.P. 90°. *p*-toluidide, M.P. 73°.	102	120
165 d.	1·288 (18°)	Pyruvic $CH_3.CO.COOH$	Sharp odour. Miscible with water, alcohol, ether. Decolourises Br-water, reduces $KMnO_4$ and ammoniacal $AgNO_3$. Forms unstable hydrazone in ether, recrystallised from alcohol, M.P. 192°. With H_2O_2, pyruvic acid gives CO_2 and acetic acid. Forms $NaHSO_3$ compound.	135	145
176	0·947 (0°)	Isovalerianic $(CH_3)_2.CH.CH_2.COOH$	Unpleasant odour. s.s. water; miscible with alcohol, ether. Ag, Zn, salts insoluble.	116	134
186	0·958 (0°)	*n*-Valerianic $CH_3(CH_2)_3.COOH$	Similar to iso-acid (B.P. 176°).	127	144
228 (15 mm.)	0·891 (12°)	Oleic $CH_3(CH_2)_7CH : CH(CH_2)_7.COOH$	Odourless. i.s. water; s. alcohol (acid reaction). Oxidised by alkaline $KMnO_4$, gives azelaic acid, M.P. 106°. Decolourises Br in CCl_4. Absorbs O_2 from air, and acquires rancid odour.	Oil $\Delta = 0·879$	Oil $\Delta = 0·871$

283. Properties of Solid Acid Anhydrides containing C.H.O only.

M.P. °C.	Name.	Characteristics.	For reactions of corresponding acid, see page
42	Benzoic $(C_6H_5.CO)_2O$	B.P. 360°. Rhombic prisms. i.s. cold water; s. alcohol, ether. Slowly decomposed by boiling water.	144
56	Maleic 	B.P. 202°. i.s. cold water. Slowly decomposed by boiling water.	145
119	Succinic 	B.P. 250°. Long needles. s.s. water; s. alcohol; i.s. ether.	147
128	Phthalic 	B.P. 284°. Fine needles. s.s. water. Fused with trace of H_2SO_4 and phenol gives phenolphthalein; fused with H_2SO_4 and resorcinol gives fluorescein.	147

284. Properties of Liquid Acid Anhydrides containing C.H.O only.

B.P. °C.	Δ	Name.	Characteristics.	For reactions of corresponding acid, see page
137	1·097 (0°)	Acetic $(CH_3.CO)_2O$	Sharp, pungent odour. s.s. water, and slowly decomposed by it. Anilide, M.P. 113°; *p*-toluidide, M.P. 146°.	149
168	1·017 (0°)	Propionic $(C_2H_5.CO)_2O$	Sharp, pungent odour. Resembles acetic anhydride. Anilide, M.P. 105°; *p*-toluidide, M.P. 124°.	149

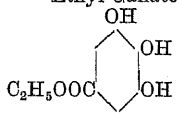
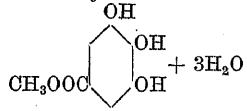
285. Properties of Solid Esters containing C.H.O only.—In the right-hand column of the table the page reference for the reactions of the corresponding acid is given.

M.P. °C.	Name.	Characteristics.	Acid. M.P. or B.P. °C.	Acid (see page)
20	Phenyl Propionate $C_2H_5.COOC_6H_5$	B.P. 211°.	B.P. 140.	149
32	Methyl *p*-Toluate $C_6H_4(CH_3).COOCH_3$		M.P. 176	146
36	Methyl Cinnamate $C_6H_5CH : CH.COOCH_3$	B.P. 260°. Unsaturated.	M.P. 133	145
42	Phenyl Salicylate o-$HO.C_6H_4.COOC_6H_5$	"Salol." $FeCl_3$ gives violet colour.	M.P. 158	146
44	Diethyl Terephthalate p-$C_6H_4(COOC_2H_5)_2$		Sublimes above 300	148
48	Dimethyl Tartrate d- $CHOH.COOCH_3$ $CHOH.COOCH_3$	B.P. 280°. Optically active.	M.P. 169	146
54	Dimethyl Oxalate $COOCH_3$ $COOCH_3$	B.P. 163°. s. water; and titrates directly with alkali. Addition of excess of strong NH_4OH to conc. aqueous solution gives oxamide.	Hydrate, M.P. 98–99	144
64	Dimethyl Isophthalate m-$C_6H_4.(COOCH_3)_2$	B.P. 280°.	M.P. above 300	148
65	Tripalmitin $CH_2OCOC_{15}H_{31}$ $CHOCOC_{15}H_{31}$ $CH_2OCOC_{15}H_{31}$	Fat. s.s. alcohol; s. ether.	M.P. 62·5	143
68	Phenyl Benzoate $C_6H_5.COOC_6H_5$	B.P. 299°.	M.P. 121	144

Properties of Solid Esters—*continued.*

M.P. °C.	Name.	Characteristics.	Acid. M.P. or B.P. °C.	Acid (see page)
70	Tristearin $C_3H_5(OCOC_{17}H_{35})$	Fat. Crystallises from ether in lustrous leaflets. s.s. alcohol.	M.P. 69·5	143
70	Diphenyl Phthalate o-C_6H_4.$(COOC_6H_5)_2$	i.s. water; s. alcohol.	M.P. 184	147
70	Methyl-*m*-oxybenzoate m-C_6H_4.(OH).$COOCH_3$	i.s. water; s. alcohol.	M.P. 200	147
72	Ethyl-*m*-oxybenzoate m-C_6H_4.(OH).$COOC_2H_5$	B.P. 282°. i.s. water; s. alcohol.	M.P. 200	147
77	Methyl β-Naphthoate β-$C_{10}H_7$.$COOCH_3$	B.P. 290°. i.s. water.	M.P. 183	146
79	Trimethyl Citrate $CH_2.COOCH_3$ | $C.OH.COOCH_3$ | CH_2COOCH_3	B.P. 285°d. i.s. water; s. alcohol.	M.P. 153	145
85	Dimethyl Racemate $CHOH.COOCH_3$ | $CHOH.COOCH_3$	B.P. 282°. i.s. water; s. alcohol.	M.P. 205	148
102	Dimethyl Fumarate $CH.COOCH_3$ || $CH.COOCH_3$	B.P. 192°. i.s. water. Unsaturated. With Br gives di-brom-succinic ester.	Sublimes 200	147
116	Ethyl-*p*-oxybenzoate p-C_6H_4(OH).$COOC_2H_5$	B.P. 270°d. i.s. water.	M.P. 210	148
131	Methyl-*p*-oxybenzoate p-C_6H_4(OH).$COOCH_3$	B.P. 298°. i.s. water.	M.P. 210	148
140	Dimethyl Terephthalate p-C_6H_4.$(COOCH_3)_2$	i.s. water.	Sublimes about 300	148

Properties of Solid Esters—*continued.*

M.P. °C.	Name.	Characteristics.	Acid. M.P. or B.P. °C.	Acid (see page)
141	Ethyl Gallate 	Hydrate, M.P. 90°.	M.P. 220–230 *d.*	148
192 *d*	Methyl Gallate 		M.P. 220–230 *d.*	148

286. Properties of Liquid Esters containing C.H.O only.

B.P. °C.	Δ (0°/4°)	Name.	Characteristics.	Acid. M.P. or B.P. °C.	Acid (see page)
32	0·998	Methyl Formate $H.COOCH_3$	Soluble in water. Saponified in the cold by alkalies.	B.P. 101	149
54	0·938	Ethyl Formate $H.COOC_2H_5$	Compare methyl ester (B.P. 32°).	B.P. 101	149
57	0·958	Methyl Acetate $CH_3.COOCH_3$	Soluble in water.	B.P. 118	149
70	0·883	Isopropyl Formate $H.COOC_3H_7$		B.P. 101	149
77	0·924	Ethyl Acetate $CH_3.COOC_2H_5$	s.s. cold water.	B.P. 118	149
80	0·937	Methyl Propionate $C_2H_5.COOCH_3$		B.P. 140	149
80	0·973	Methyl Acrylate $CH_2 : CH.COOCH_3$	Unsaturated.	B.P. 140	149

Properties of Liquid Esters—*continued.*

B.P. °C.	Δ (0°/4°)	Name.	Characteristics.	Acid. M.P. or B.P. °C.	Acid (see page)
81	0·918	*n*-Propyl Formate $H{\cdot}COOC_3H_7$		B.P. 101	149
91	0·917	*iso*-Propyl Acetate $CH_3.COOC_3H_7$		B.P. 118	149
91	1·065 (17°)	Dimethyl Carbonate $OC:(OCH_3)_2$		—	—
92	0·912	Methyl *iso*-Butyrate $C_3H_7.COOCH_3$		B.P. 155	149
98	0·912	Ethyl Propionate $C_2H_5.COOC_2H_5$		B.P. 140	149
98	0·939	Ethyl Acrylate $CH_2:CH.COOC_2H_5$	Unsaturated.	B.P. 140	149
102	0·909	*n*-Propyl Acetate $CH_3.COOC_3H_7$		B.P. 118	149
102	0·919	Methyl Butyrate $C_3H_7.COOCH_3$		B.P. 162	150
103	0·938	Allyl Acetate $CH_3.COOCH_2.CH:CH_2$	Sharp odour.	B.P. 118	149
110	0·890	Ethyl *iso*-Butyrate $C_3H_7.COOC_2H_5$		B.P. 155	149
116	0·892	*iso*-Butyl Acetate $CH_3.COOC_4H_9$		B.P. 118	149
116	0·901	Methyl *iso*-Valerianate $C_4H_9.COOCH_3$		B.P. 176	150
120	0·900	Ethyl Butyrate $C_3H_7.COOC_2H_5$		B.P. 162	150

Properties of Liquid Esters—*continued.*

B.P. °C.	Δ (0°/4°)	Name.	Characteristics.	Acid. M.P. or B.P. ° C.	Acid (see page)
125	0·902	Butyl Acetate $CH_3.COOC_4H_9$		B.P. 118	149
126	0·976 (20°)	Diethyl Carbonate $OC:(OC_2H_5)_2$		—	—
127	0·910	Methyl Valerianate $C_4H_9.COOCH_3$		B.P. 186	150
134	0·885	Ethyl *iso*-Valerianate $C_4H_9.COOC_2H_5$		B.P. 176	150
135	1·154	Methyl Pyruvate $CH_3.CO.COOCH_3$	Decomposed by cold water.	B.P. 165	150
139	0·884	*iso*-Amyl Acetate $CH_3.COOC_5H_{11}$	Odour of pears.	B.P. 118	149
144	0·894	Ethyl Valerianate $C_4H_9.COOC_2H_5$		B.P. 186	150
145	1·118	Methyl Lactate $CH_3.CHOH.COOCH_3$	Soluble in water, acid in reaction.	M.P. 18 B.P. 119 (12 mm.)	143
148	0·896	Amyl Acetate $CH_3.COOC_5H_{11}$		B.P. 118	149
151	1·187	Methyl Glycollate $\begin{matrix}CH_2OH\\ \vert\\ COOCH_3\end{matrix}$		M.P. 78	144
154	1·055	Ethyl Lactate $CH_3.CHOH.COOC_2H_5$	Soluble in water. Acid in reaction.	M.P. 18 B.P. 119 (12 mm.)	143

Properties of Liquid Esters—*continued.*

B.P. °C.	Δ (0°/4°)	Name.	Characteristics.	Acid. M.P. or B.P. °C.	Acid (see page)
160	1·108	Ethyl Glycollate $\begin{matrix}CH_2OH\\ \vert\\ COOC_2H_5\end{matrix}$		M.P. 78	144
170	1·037 (9°)	Methyl Acetoacetate $CH_3.CO.CH_2.COOCH_3$	Soluble in water. $FeCl_3$ gives bright red colour. Saponified with aqueous NaOH gives CH_3OH+ CH_3COCH_3	—	—
180	1·046	Ethyl Acetoacetate $CH_3.CO.CH_2.COOC_2H_5$	Soluble in aqueous alkalies. Red colour with $FeCl_3$. Saponified with aqueous NaOH, gives alcohol, CO_2, and acetone.	—	—
181	1·175	Dimethyl Malonate $CH_2(COOCH_3)_2$	Decolourises Br-water.	M.P. 132	145
186	1·082 (18°)	Diethyl Oxalate $\begin{matrix}COOC_2H_5\\ \vert\\ COOC_2H_5\end{matrix}$	Soluble in water. Acid in reaction; immediately saponified with alkalies. Strong NH_4OH gives immediate precipitate of oxamide.	M.P. 98–99	144
187	1·010	Ethyl Methylacetoacetate $CH_3CO.CH(CH_3).COOC_2H_5$	Insoluble in cold NaOH. Blue colour with $FeCl_3$. Saponification with alcoholic NaOH gives methyl ethyl ketone, ethyl alcohol and CO_2.	—	—

Properties of Liquid Esters—*continued.*

B.P. °C.	Δ (0°/4°)	Name.	Characteristics.	Acid. M.P. or B.P. °C.	Acid (see page)
189	0·995 (14°)	Methyl Ethylacetoacetate $CH_3CO.CH(C_2H_5).COOCH_3$	Insoluble in cold NaOH. Violet colour with $FeCl_3$. Saponification with alcoholic NaOH gives methyl propyl ketone.	—	—
195	1·126 (15°)	Dimethyl Succinate $CH_2.COOCH_3$ | CH_2COOCH_3	M.P. 19°. Soluble in cold water.	M.P. 185	147
196	1·093	Phenyl Acetate $CH_3.COOC_6H_5$		B.P. 118	149
198	0·998 (12°)	Ethyl Ethylacetoacetate $CH_3CO.CH(C_2H_5).COOC_2H_5$	Compare with the methyl ester (B.P. 189).	—	—
198	1·077	Diethyl Malonate $CH_2(COOC_2H_5)_2$	Decolourises Br-water.	M.P. 132	145
199	1·103	Methyl Benzoate $C_6H_5.COOCH_3$		M.P. 121	144
205	1·153 (14°)	Dimethyl Maleate $CH.COOCH_3$ ‖ $CH.COOCH_3$	Unsaturated.	M.P. 130	145
206	1·057 (16°)	Benzyl Acetate $CH_3.COOCH_2.C_6H_5$		B.P. 118	149
211	1·054 (15°)	Phenyl Propionate $C_2H_5.COOC_6H_5$	M.P. 20°.	B.P. 140	149
212	1·066	Ethyl Benzoate $C_6H_5.COOC_2H_5$		M.P. 121	144

Properties of Liquid Esters—*continued.*

B.P. °C.	Δ (0°/4°)	Name.	Characteristics.	Acid. M.P. or B.P. °C.	Acid (see page)
216	1·072	Diethyl Succinate $CH_2.COOC_2H_5$ | $CH_2.COOC_2H_5$	Soluble in water.	M.P. 185	147
218	1·063 (10°)	Diethyl Fumarate $CH.COOC_2H_5$ ‖ $CH.COOC_2H_5$	Unsaturated.	Sublimes 200	147
220	1·044 (16°)	Methyl Phenylacetate $C_6H_5.CH_2.COOCH_3$		M.P. 76	143
221	—	Ethyl *o*-Toluate o-$C_6H_4(CH_3)COOC_2H_5$		M.P. 102	144
224	1·197	Methyl Salicylate o-$HO.C_6H_4.COOCH_3$	Violet colour with $FeCl_3$. Odour of Oil of Wintergreen	M.P. 158	146
225	1·074 (15°)	Diethyl Maleate $CH.COOC_2H_5$ ‖ $CH.COOC_2H_5$	Unsaturated.	M.P. 130	145
227	—	Ethyl *m*-Toluate m-$CH_3.C_6H_4.COOC_2H_5$		M.P. 110	144
228	—	Ethyl *p*-Toluate p-$CH_3.C_6H_4.COOC_2H_5$		M.P. 176	146
229	1·086 (16°)	Ethyl Phenylacetate $C_6H_5.CH_2.COOC_2H_5$		M.P. 76	143
231	1·147 (4°)	Ethyl Salicylate o-$C_6H_4(OH)COOC_2H_5$	Violet colour with $FeCl_3$. Odour of Oil of Wintergreen	M.P. 158	146
271	1·066	Ethyl Cinnamate $C_6H_5.CH : CH.COOC_2H_5$	M.P. 12°. Unsaturated.	M.P. 133	145

Properties of Liquid Esters—*continued.*

B.P. °C.	Δ (0°/4°)	Name.	Characteristics.	Acid. M.P. or B.P. °C.	Acid (see page)
280	1·206 (20°)	Diethyl *d*-Tartrate $CHOH.COOC_2H_5$ | $CHOH.COOC_2H_5$	Optically active.	M.P. 169	146
282	—	Dimethyl Phthalate o-$C_6H_4(COOCH_3)_2$		M.P. 184	147
285	—	Dimethyl *iso*-Phthalate m-$C_6H_4(COOCH_3)_2$		M.P. above 300	148
294	1·137 (20°)	*Tri*-Ethyl Citrate $CH_2.COOC_2H_5$ | $C(OH)COOC_2H_5$ | $CH_2.COOC_2H_5$		M.P. 153	145
295	1·118 (20°)	Diethyl Phthalate o-$C_6H_4(COOC_2H_5)_2$		M.P. 184	147
308	—	Ethyl β-Naphthoate β-$C_{10}H_7.COOC_2H_5$		M.P. 183	146
309	—	Ethyl α-Naphthoate α-$C_{10}H_7.COOC_2H_5$		M.P. 160	146
323	1·114 (18°)	Benzyl Benzoate $C_6H_5.COOCH_2.C_6H_5$		M.P. 121	144

THE IDENTIFICATION OF PHENOLS AND PHENOLIC COMPOUNDS

287. General Remarks.—In the colour reaction with ferric chloride, yellow or orange-yellow tones may be neglected. All liquid phenolic compounds answer to this test, but a few solid phenols do not give a pronounced colour with this reagent. These latter compounds are, however, soluble in aqueous caustic soda, although not appreciably soluble in water.

Many phenolic compounds dissolve in alkali with the production of brilliant colours, *e.g.*, the phthaleins, whilst in some other cases the solutions turn brown owing to rapid oxidation, due to absorption of free oxygen, *e.g.*, pyrogallol.

Only a few of the simpler phenols, such as phenol, resorcinol, and pyrogallol, are soluble in water. Many possess characteristic odours. Some reduce alkaline permanganate, and the majority of the poly-hydric phenols precipitate metallic silver from Tollen's reagent (see paragraph **514**). Since the phenolic group greatly facilitates nucleus substitution, phenols are readily nitrated or brominated, giving precipitates on treatment with an excess of bromine water. A few phenols, such as α-naphthol, are oxidised by ferric chloride with the formation of crystalline precipitates.

The characteristic properties of the solid phenolic compounds are given in paragraph **288**, and those of liquid phenolic compounds in paragraph **289**, page 166.

288. Properties of Solid Phenolic Compounds containing C.H.O only.

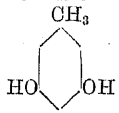
. = blue, V. = violet, R. = red, O. = orange, Y. = yellow, G. = green.

M.P. °C.	Colour with $FeCl_3$.	Name.	Characteristics.
30	B.V. transient, then Y. G.B. in alcohol.	*o*-Cresol o-$CH_3.C_6H_4.OH$	B.P. 191°. Dibrom-derivative, M.P. 56°. Oxidation with alkaline $KMnO_4$ gives salicylic acid, M.P. 158°. i.s. in strong NH_4OH.

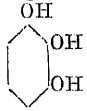
Properties of Solid Phenolic Compounds—*continued.*

M.P. °C.	Colour with $FeCl_3$.	Name.	Characteristics.
31	R.O. becomes turbid, G.B. in alcohol.	Guaiacol o-$CH_3O.C_6H_4.OH$	B.P. 205°. s.s. water. Picrate precipitated in aqueous solution after two minutes' standing, M.P. 86°. Benzoyl derivative, M.P. 57°.
36	B.—B.V. becomes turbid.	p-Cresol p-$CH_3.C_6H_4.OH$	B.P. 202°. Tetrabrom-derivative, M.P. 108°*d*. Oxidation with alkaline $KMnO_4$ gives p-oxy-benzoic acid, M.P. 210°. Benzoyl derivative, M.P. 71°. i.s. in strong NH_4OH.
42	V.R.	Phenyl Salicylate.	See page 152.
42–3	V.	Phenol C_6H_5OH	B.P. 183°. s. water, alcohol, NaOH. i.s. Na_2CO_3 solution; s. in 5 parts strong ammonia. (Contrast the cresols.) Nitrated with dilute HNO_3 gives odour of o-nitrophenol. Br-water gives tribrom-derivative, M.P. 93°. Fusion with phthalic anhydride and 1 drop H_2SO_4 gives phenolphthalein, M.P. 250°.
49	G. in conc. alcoholic solution. Transient.	Thymol $CH.(CH_3)_2$  CH_3	B.P. 232°. Characteristic odour. s.s. water. Benzoyl derivative, M.P. 32°. Fused with phthalic anhydride and 1 drop H_2SO_4 gives V.R. mass soluble in NaOH with B. colour. Nitrated on water bath with conc. HNO_3 and conc. H_2SO_4 gives trinitro-compound, M.P. 109°.
58	B.V.	Orcinol+$1H_2O$	See Orcinol (M.P. 107°).
80	B.	Vanillin	See page 135.
86	R.V.–Y.O.	Saligenin o-$HO.C_6H_4.CH_2OH$	Rhombic crystals. Sublimes. s. water, alcohol. Gives R. colour with conc. H_2SO_4 on stirring.

Properties of Solid Phenolic Compounds—*continued.*

M.P. °C.	Colour with $FeCl_3$.	Name.	Characteristics.
94	Scanty white precipitate.	α-Naphthol α-$C_{10}H_7.OH$	B.P. 279°. Monoclinic crystals. Characteristic odour. s.s. hot water; s. alcohol, ether. Boil 0·1 gm. with 15 c.c. of 1 per cent. NaOH solution and 10 drops of $CHCl_3$ for 30 seconds. A clear blue liquid changing to bluish green is formed. Picrate, from dilute alcohol, M.P. 188°. Benzoyl derivative, M.P. 56°.
104	G. on adding Na_2CO_3 gives R.–O.R.	Catechol o-$C_6H_4(OH)_2$	B.P. 242°. e.s. water, alcohol. Easily oxidised. Alkaline solution darkens in air. Reduces Fehling's solution. Benzoyl derivative, M.P. 84°. White precipitate with Pb acetate.
107	V.B.	Orcinol 	Hydrate, $+1H_2O$, M.P. 58°. B.P. 287°. e.s. water, alcohol. Solution in ammonia turns red on exposure to air. Reduces Tollen's solution (**514**). Br-water precipitates tribrom-compound, M.P. 98°. Benzoyl derivative, M.P. 84°. Boiled with 1 per cent. NaOH solution and $CHCl_3$, gives O.–O.R. colour.
116	B.V.	Resorcinol m-$C_6H_4(OH)_2$	B.P. 276°. v.s. water, alcohol. Fused with phthalic acid and 1 drop of H_2SO_4 gives fluorescein, which forms a red solution in NaOH with vivid green fluorescence. Dissolved in conc. H_2SO_4 and nitrated in the cold with H_2SO_4 and HNO_3 the trinitro-compound is formed, M.P. 195°. Boiled with 1 per cent. NaOH solution and $CHCl_3$, a red fluorescent solution is formed. Benzoyl derivative, M.P. 117°.

Properties of Solid Phenolic Compounds—*continued.*

M.P. °C.	Colour with $FeCl_3$.	Name.	Characteristics.
116	—	Benzoquinone p-$C_6H_4O_2$	Golden yellow. Pungent odour. s.s. water, but easily soluble in alkalies, the solution turning brown on exposure to air. See page 169.
122	White opalescence.	β-Naphthol β-$C_{10}H_7$.OH	B.P. 285°. s.s. hot water; e.s. alcohol, ether. Boiled 30 seconds with 1 per cent. NaOH + 5 drops of $CHCl_3$ gives B. colour, then G. to Y. and colourless in 10 minutes. The picrate, precipitated from dilute alcohol, M.P. 156°. Benzoyl derivative, M.P. 107°.
133	O.R.	Pyrogallol 	B.P. 293°*d.* e.s. water, alcohol. Alkaline solution turns brown in the air. Blue precipitate with $FeSO_4$. Reduces $AgNO_3$. Benzoyl derivative, M.P. 89°. Boiled with acetic anhydride and anhydrous sodium acetate, gives triacetate, M.P. 161°.
144	B.V. transient.	Arbutin $C_{25}H_{34}O_{14}$	s. hot water, alcohol; e.s. NaOH solution. Soluble in conc. H_2SO_4 with a red colour (glucoside). Boiled with excess of $FeCl_3$, the pungent odour of quinone is smelt. Hydrolysed by dilute H_2SO_4, hydroquinone and dextrose are formed. Penta-benzoyl derivative, M.P. 160°.
158	R.V.	Salicylic Acid	See page 146.
169	Y.O.	Quinol Hydroquinone p-$C_6H_4(OH)_2$	Sublimes. s. water, alcohol; i.s. benzene. Boiled with excess of $FeCl_3$, the sharp odour of quinone is given. The alkaline solution turns brown on exposure to air. Reduces $AgNO_3$ and Fehling's solution. Oxidised in the cold by acid $K_2Cr_2O_7$ to quinhydrone, M.P. 170°. Benzoyl derivative, M.P. 199°.

Properties of Solid Phenolic Compounds—*continued.*

M.P. °C.	Colour with $FeCl_3$.	Name.	Characteristics.
175	—	Helicine	See page 135.
180	—	Populin Benzoyl Salicin $C_{20}H_{22}O_8+2H_2O$	i.s. cold water; s.s. hot water. Soluble in strong alkalies. Conc. H_2SO_4 gives red colour (glucoside). Lævo-rotatory. Saponified with $Ba(OH)_2$ gives salicin and benzoic acid.
185.	—	Coniferin $C_{16}H_{22}O_8+2H_2O$	i.s. cold water; s. alkalies, hot water. Warmed with conc. HCl turns blue. Warmed with conc. H_2SO_4 gives V.R. solution (glucoside). Hydrolysis with acid gives dextrose and coniferyl alcohol. Benzoyl derivative, M.P. 80°.
201	—	Salicin $C_{13}H_{18}O_7$	s. hot water, hot alcohol, alkalies. Lævo-rotatory. Is a glucoside. Red colour with conc. H_2SO_4. Reduces ammoniacal $AgNO_3$. With Br-water gives brom-derivative, M.P. 170°. Hydrolysed by dilute H_2SO_4 gives dextrose and saliretin.
210	Y. precipitate.	*p*-Oxybenzoic Acid	See page 148.
218	B.V.–V. fades readily.	Phloroglucinol 2 : 4 : 6-$C_6H_3(OH)_3$ $+2H_2O$	Loses $2H_2O$ at 100°. Sublimes. e.s. water, alcohol. Solution in alkalies slowly absorbs oxygen. Pine-splinter soaked in conc. HCl and dipped in solution gives deep-red colour. Br-water gives tribrom-derivative, M.P. 151°. Benzoyl derivative, M.P. 173°. Nitrated in the cold with conc. $H_2SO_4+HNO_3$ gives trinitro-compound, M.P. 165°.
218	G. Bright R. on heating.	β-Dinaphthol β-$(C_{10}H_6.OH)_2$	i.s. water; s. alcohol, ether. On distillation gives β-naphthol. Picrate, M.P. 174°.

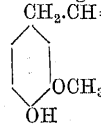
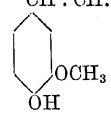
Properties of Solid Phenolic Compounds—*continued.*

M.P °C.	Colour with $FeCl_3$.	Name.	Characteristics.
220–40	B. precipitate.	Gallic Acid	See page 148.
250	—	Phenolphthalein $C_{20}H_{14}O_4$	i.s. water; s. alcohol. s. in NaOH with intense red colour, which is discharged by large excess of NaOH or on the addition of Zn dust and warming.
289	—	Alizarine $C_{14}H_8O_4$	Orange colour. i.s. water; e.s. alkalies with production of purple colour. See page 170.
300	V.R. precipitate.	α-Dinaphthol α-$(C_{10}H_6.OH)_2$	i.s. water; s. alcohol; e.s. ether.

289. Properties of Liquid Phenolic Compounds. C.H.O only.

B.P. °C.	Δ	Colour with $FeCl_3$.	Name.	Characteristics.
139	0·987 (15°)	O.R.	Acetyl Acetone $CH_3COCH_2COCH_3$	s.s. water; distinctly acid. Heavy blue precipitate with copper acetate solution. Hydrolysed by alcoholic potash to acetic acid and acetone.
170		R.	Methyl Acetoacetate	See page 157.
180		R.	Ethyl Acetoacetate	See page 157.
187		B.	Ethyl Methylacetoacetate	See page 157.
189		V.R.	Methyl Ethylacetoacetate	See page 158.
196		V.	Salicyl Aldehyde	See page 136.
198		B.	Ethyl Ethylacetoacetate	See page 158.

Properties of Liquid Phenolic Compounds—*continued.*

B.P. °C.	Δ	Colour with $FeCl_3$.	Name.	Characteristics.
203	1·050	B.V.	*m*-Cresol *m*-$CH_3.C_6H_4.OH$	s. water. Odour of phenol. Insoluble in 5 parts conc. NH_4OH. Heated on water bath for 10 minutes with conc. H_2SO_4 and HNO_3 gives trinitro-compound, M.P. 106°. Oxidised by alkaline $KMnO_4$ to *m*-oxybenzoic acid, M.P. 200°. Benzoyl derivative, M.P. 54°.
224		R.V.	Methyl Salicylate	See page 159.
231		R.V.	Ethyl Salicylate	See page 159.
247	1·063 (18°)	Y.G. but B. in alcohol.	Eugenol $CH_2.CH=CH_2$  OCH_3 OH	Odour of cloves. s.s. water; e.s. alcohol, ether. Unsaturated. Oxidised with alkaline $KMnO_4$ gives vanillin and vanillic acid. Benzoyl derivative, M.P. 69°.
260	1·080 (16°)	G. in alcohol.	Iso-Eugenol $CH : CH.CH_3$  OCH_3 OH	s.s. water; s. alcohol, ether. Unsaturated. Solidifies in a freezing mixture. Benzoyl derivative, M.P. 103°.

IDENTIFICATION OF KETONES

290. General Remarks.—In addition to yielding phenylhydrazones on treatment with phenylhydrazine in acetic acid solution, ketones readily form oximes. The ketoximes are best prepared by using a solution of hydroxylamine hydrochloride in aqueous alcohol in the presence of rather more than an equivalent quantity of aqueous alcoholic sodium hydroxide (see preparation 31, page 55). The oximes of the ketones are formed less readily than those of the aldehydes, in the former case the reactants should therefore be warmed on the water bath for a few minutes. The mixture is then cooled, diluted with water, and the oxime recrystallised. In a few cases it is necessary to heat the reaction mixture for an hour or two to obtain a satisfactory yield.

The ketones as a class are less readily oxidised than the aldehydes. They do not, in general, reduce Fehling's solution or ammoniacal silver nitrate, nor do they restore the colour to a solution of decolourised magenta. Aliphatic ketones, such as acetone or acetophenone, are readily halogenated in the group adjacent to the keto-group :

$$CH_3 . CO . C_6H_5 + Br_2 \rightarrow CH_2Br . CO . C_6H_5 + HBr.$$

With phosphorus pentachloride they give dichlor-derivatives :

$$R . CO . R' + 2PCl_5 \rightarrow R . CCl_2 . R' + 2POCl_3.$$

Ketones containing the grouping $CH_3 . CO$— give characteristic colour reactions on treatment in aqueous solution with sodium nitroprusside and a trace of alkali.

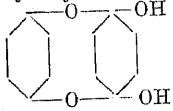
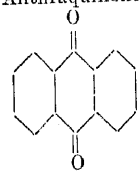
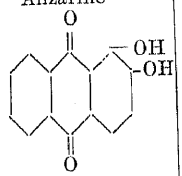
291. Properties of Solid Ketones containing C.H.O only.

M.P. °C.	Name.	Characteristics.	M.P. Phenylhydrazone. °C.	M.P. Oxime. °C.
20	Acetophenone $CH_3{\cdot}CO{\cdot}C_6H_5$	See Liquid Ketones (B.P. 202°).		
28	Phorone $C_9H_{14}O$	B.P. 198°. Unsaturated. Peculiar odour. Pale yellow crystals. With Br in CCl_4 gives tetrabrom-derivative, M.P. 88°.		48

Properties of Solid Ketones—*continued.*

M.P. °C.	Name.	Characteristics.	M.P. Phenylhydrazone. °C.	M.P. Oxime. °C.
42	Benzalacetone $CH_3CO.CH{:}CH.C_6H_5$	B.P. 260°. i.s. water; e.s. alcohol, ether. Pale yellow. Unsaturated. Soluble in conc. H_2SO_4 with orange colour. Acid $KMnO_4$ gives benzaldehyde. Dibromide, M.P. 124°.	156	115
48	Benzophenone $C_6H_5.CO.C_6H_5$	B.P. 305°. i.s. water; e.s. alcohol, ether. Gently heated with metallic Na gives dark blue colour.	137	141
51	Methyl-β-naphthyl Ketone. β-$C_{10}H_7.CO.CH_3$	B.P. 300°. i.s. water. White needles. With Br in CCl_4 gives dibrom-compound. M.P. 101°.		142
59	Phenyl-*p*-tolyl Ketone *p*-$C_6H_5.CO.C_6H_4.CH_3$	i.s. water; e.s. alcohol, ether.		153 115 Isomeric.
95	Benzil $C_6H_5.CO.CO.C_6H_5$	B.P. 346°. Pale yellow colour. i.s. water; e.s. alcohol, ether. Dissolved in absolute alcohol, with one fourth its weight of KOH, gives V.R. colour on evaporation on water bath. Alkaline $KMnO_4$ gives benzoic acid, M.P. 121°.	225	Isomeric. solids.
116	Benzoquinone *p*-$C_6H_4O_2$	Golden-yellow colour. Pungent odour. Sublimes. s.s. water; e.s. alcohol, ether. Solution in alkalies absorbs O_2 and turns brown. Boiled with excess of aniline dissolved in alcohol gives a di-anil, V.R. colour, sublimes at 235°. Reduced by H_2SO_3 to quinhydrone, M.P. 171° (see page 170).	—	240 *d.*
133	Benzoin $C_6H_5.CO.CHOH.C_6H_5$	B.P. 343°. Usually pale yellow colour. i.s. water; s. alcohol. Oxidised by HNO_3 to benzil, M.P. 95°, and by acid $KMnO_4$ to benzaldehyde and benzoic acid, M.P. 121°. Heated with acetyl chloride gives acetyl compound, which on crystallisation from aqueous alcohol has M.P. 80°.	106	151

Properties of Solid Ketones—*continued.*

M.P. °C.	Name.	Characteristics.	M.P. Phenylhydrazone. °C.	M.P. Oxime. °C.
171	Quinhydrone 	Dark green, metallic lustre ; reddish by transmitted light. Sublimes. s.s. water (brown solution) ; e.s. alcohol, ether (green solution). Boiled with water gives quinone and hydroquinone. Reduced by H_2SO_3 to quinol. Reduces ammoniacal $AgNO_3$.	—	—
176	Camphor $C_{10}H_{16}O$	B.P. 205°. Penetrating characteristic odour. White, translucent, tough, crystalline. Small pieces rapidly move about when thrown on water. Very volatile in steam. v.s.s. water ; s. alcohol, ether. Natural camphor $[\alpha]_D = +44{\cdot}2$ in alcohol. Synthetic camphor inactive.	B.P. 230	118 formed but slowly.
275	Anthraquinone 	B.P. 380°. Pale yellow colour. Sublimes. i.s. water ; s.s. alcohol, ether. Very stable. Heated with Zn dust gives anthracene. Boiled with aqueous NaOH and Zn dust gives deep red solution, which absorbs O_2 from air and is decolourised again.	—	—
289	Alizarine 	B.P. 430°. Orange colour. i.s. water ; v.s.s. alcohol, ether. Easily soluble in dilute alkalies, giving a purple solution, from which blue Ca or Ba salts are readily precipitated. Readily forms colour lakes with Sn, Cr, Fe, Al. Soluble in conc. H_2SO_4 with purple colour. Nitrated in glacial acetic acid solution gives 3-nitro-derivative, M.P. 244°.	—	—

292. Properties of Liquid Ketones containing C.H.O only.

B.P. °C.	Δ 0°C.	Name.	Characteristics.	M.P. of phenyl-hydra-zone. °C.	M.P. of oxime. °C.
56	0·819	Acetone $CH_3.CO.CH_3$	Miscible with water, alcohol, ether. Nitroprusside test gives a red colour. Yields iodoform with NaOH and iodine. Forms the bisulphite compound readily.		60
80	0·830	Methyl Ethyl Ketone $CH_3.CO.C_2H_5$	Miscible with water, alcohol. Resembles acetone.	Liquid.	B.P. 152
88	0·975 (20°)	Diacetyl $CH_3CO.COCH_3$	Yellow liquid, pronounced odour. s. water. Soluble in alkali, giving opaque brown solution.		234
103	0·834	Diethyl Ketone $C_2H_5.CO.C_2H_5$	s.s. water. Oxidised with CrO_3 gives acetic and propionic acids.	Liquid.	B.P. 165
106	0·826	Pinacoline $CH_3.CO.C(CH_3)_3$	Peppermint odour. i.s. water. Oxidised with CrO_3 and H_2SO_4 gives trimethyl-acetic acid, M.P. 35°.	Liquid.	74
130	0·858 (20°)	Mesityl Oxide $(CH_3)_2C:CH.CO.CH_3$	Peppermint odour. i.s. water; v.s. alcohol. Boiled with dilute H_2SO_4 gives acetone. Unsaturated.	Oil.	49
139	0·987 (15°)	Acetyl Acetone $CH_3.CO.CH_2.CO.CH_3$	See page 166.		
202	1·032 (15°)	Acetophenone $CH_3.CO.C_6H_5$	M.P. 20°. Almost i.s. water. Oxidised with alkaline $KMnO_4$ gives benzoic acid, M.P. 121°. Nitroprusside test gives reddish violet colour, changing to blue when acidified with acetic acid.	103	59

Properties of Liquid Ketones—*continued.*

B.P. °C.	Δ 0°C.	Name.	Characteristics.	M.P. of phenyl-hydra-zone. °C.	M.P. of oxime. °C.
207	0·896 (20°)	*l*-Menthone $C_{10}H_{18}O$	Peppermint odour. s.s. water. Miscible with alcohol, ether. Lævo-rotatory, $[\alpha]_D$ = −28·2°.		118
222	1·013	*p*-Methyl Tolyl Ketone *p*-$CH_3.CO.C_6H_4.CH_3$	i.s. water. Alkaline $KMnO_4$ gives terephthalic acid, which sublimes above 300°. Di-brom-derivative, M.P. 100°.		

THE IDENTIFICATION OF ALCOHOLS CONTAINING C.H.O ONLY

293. General Remarks.—Any compound which has not responded to any of the generic tests for the classes of organic compounds already described, and which is sparingly soluble in water, necessarily belongs to this section. As shown on page 133, the alcohols react with sodium with the evolution of hydrogen. The presence of an alcohol may also be shown by the quantitative estimation of the loss of acetic anhydride on acetylation, details of which process are given in the Quantitative Section in paragraphs **447, 448.** It is not usually necessary to carry out this estimation in order to prove the substance to be an alcohol.

The alcohol under examination may be identified by the physical properties of derived esters, particularly the acetates and benzoates.

A number of the more volatile alcohols, as well as acetone, form iodoform on warming with dilute NaOH solution and a few crystals of iodine to about 60°. This test serves to distinguish a number of the alcohols, as shown in paragraph **295.**

294. Properties of Solid Alcohols containing C.H.O only.

M.P. °C.	Name.	Characteristics.	Acetate. °C.	Benzoate. °C.
25	Tertiary Butyl Alcohol	See page 175.		
35	Terpineol	See page 176.		
35	Pinacone $(CH_3)_2=C-OH$ / $(CH_3)_2=C-OH$	B.P. 172°. Faint odour. Soluble in water; hot solution deposits hydrate, M.P. 56°. Boiled with dilute H_2SO_4 gives pinacoline (peppermint odour).		
42	*l*-Menthol $C_{10}H_{19}OH$	B.P. 212°. Characteristic odour, somewhat like peppermint. s.s. water; e.s. alcohol and conc. HCl. $[\alpha]_D = -59{\cdot}6$ in alcohol.	B.P. 227	M.P. 54
56	Pinacone Hydrate $C_6H_{14}O_2+6H_2O$	Sublimes. Distilled gives pinacone, M.P. 35°. See above.		

Properties of Solid Alcohols—*continued.*

M.P. °C.	Name.	Characteristics.	Acetate. °C.	Benzoate. °C.
148	Cholesterol $C_{26}H_{43}OH+H_2O$	s.s. alcohol; e.s. ether. Dissolved in $CHCl_3$ and shaken with conc. H_2SO_4 gives reddish purple $CHCl_3$ layer and green fluorescence in the acid layer. The benzoate melts at 145° to a turbid liquid, which clears at about 179°. On cooling opalescent colours are exhibited, including both blue and violet.	M.P. 114	M.P. 145
166	*d*-Mannitol CH_2OH | $CHOH_4$ | CH_2OH	Crystalline needles. s. water; v.s.s. absolute alcohol, ether. Only exhibits pronounced optical activity in borax solution. Prevents precipitation of iron from $FeCl_3$ by NaOH.	M.P. 119	M.P. 124
203	*d*-Borneol $C_{10}H_{17}OH$	Odour of camphor. B.P. 211°. Sublimes. Almost i.s. water; e.s. alcohol, ether. $[\alpha]_D = +37°$ in alcohol. Oxidised by HNO_3 gives camphor.	M.P. 29 B.P. 221	M.P. 25

295. Properties of Liquid Alcohols containing C.H.O only.

B.P. °C.	Δ 0°C.	Name.	Characteristics.	Acetate. °C.	Benzoate. °C.
35	0·719 (15°)	Diethyl Ether $C_2H_5.O.C_2H_5$	See page 179.		
66	0·798 (15°)	Methyl Alcohol CH_3OH	Alcoholic odour. Miscible with water. Oxidised by hot Cu wire, covered with oxide, to H.CHO; after oxidation cool the test tube, add 1 or 2 drops of a dilute solution of resorcin, and pour the whole slowly on to 5 c.c. of conc. H_2SO_4 in another tube. A reddish-violet ring is produced, with the gradual formation of a reddish precipitate in the aqueous layer.	B.P. 57	B.P. 199

Properties of Liquid Alcohols—*continued.*

B.P. °C.	Δ 0°C.	Name.	Characteristics.	Acetate. °C.	Benzoate. °C.
78	0·794 (15°)	Ethyl Alcohol C_2H_5OH	Alcoholic odour. Miscible with water. Gives iodoform with NaOH and I_2 at 60°C. Oxidised by CrO_3 to acetaldehyde.	B.P. 77	B.P. 212
83	0·789 (20°)	Isopropyl Alcohol $CH_3.CHOH.CH_3$	Miscible with water. Gives iodoform reaction in the cold. Oxidised by CrO_3 and H_2SO_4 to acetone.	B.P. 91	B.P. 218 *d.*
83	0·780 (26°)	Tertiary Butyl Alcohol $(CH_3)_3COH$	M.P. 25°. Mild alcoholic odour. v.s. water. Does not give iodoform reaction.	B.P. 96	—
96	0·871	Allyl Alcohol $CH_2 : CH.CH_2OH$	Powerful odour. Miscible with water. Unsaturated. Oxidised to acrolein by CrO_3. Gives a small amount of iodoform with NaOH and I_2 at 60°.	B.P. 103 sharp odour	B.P. 230
97	0·804 (20°)	*n*-Propyl Alcohol $C_2H_5.CH_2OH$	Mild odour. Miscible with water. Does not yield iodoform.	B.P. 102	B.P. 230
100	0·827	*sec*-Butyl Alcohol $CH_3.CH_2.CHOH.CH_3$	Miscible with water. Oxidised with CrO_3 to methyl ethyl ketone. Forms iodoform in the cold with NaOH and I_2.	B.P. 111	
102	0·814 (15°	Tertiary Amyl Alcohol $(CH_3)_2.C.(OH).C_2H_5$	Mild odour. Not v.s. water. Does not give iodoform.	B.P. 124	—
106	0·817	*iso*-Butyl Alcohol $(CH_3)_2.CH.CH_2OH$	Mild odour. Soluble in 10 parts water.	B.P. 116	B.P. 237
117	0·810 (20°)	Butyl Alcohol $C_4H_9.OH$	Mild odour. Soluble in 12 parts water.	B.P. 125	B.P. 247

Properties of Liquid Alcohols—*continued.*

B.P. °C.	Δ 0°C.	Name.	Characteristics.	Acetate. °C.	Benzoate. °C.
130	0·810 (20°)	Isoamyl Alcohol $(CH_3)_2.CH.CH_2CH_2OH$	Disagreeable odour. s.s. water. Warmed with conc. H_2SO_4 gives red solution. Warmed with CrO_3 and H_2SO_4 gives a pleasant odour of valeric aldehyde, followed by the disgusting odour of the acid.	B.P. 139 odour of pears.	B.P. 261
198	1·125	Ethylene Glycol CH_2OH CH_2OH	Somewhat viscous. Miscible with water. s.s. ether. Heated strongly with solid $KHSO_4$ gives acetaldehyde. Compare glycerine (B.P. 290°).	B.P. 186	M.P. 73
205	1·043 (20°)	Benzyl Alcohol $C_6H_5.CH_2OH$	Faint aromatic odour. s.s. water. Oxidised by alkaline $KMnO_4$ to benzoic acid, M.P. 121°.	B.P. 206	B.P. 323
218	0·936 (20°)	Terpineol $C_{10}H_{18}O$	Odour of lilac on dilution. Dextrorotatory $[\alpha]_D = 117·5°$ in alcohol. Separates from ether as a solid, M.P. 35°. i.s. water. Unsaturated. Dibromide forms as an oily liquid. With HCl gives hydrochloride, M.P. 50°.	B.P. 195	—
229	0·880 (15°)	Geraniol $C_{10}H_{18}O$	Odour of geranium. i.s. water; miscible with alcohol. Optically inactive. Oxidised by alkaline $KMnO_4$ gives acetone and lævulinic acid. Forms a crystalline derivative with solid $CaCl_2$.	B.P. 242*d*. Pleasant smell.	—
290	1·260 (20°)	Glycerol CH_2OH | $CHOH$ | CH_2OH	Viscous syrup. Hygroscopic. Miscible with water, alcohol. i.s. dry ether. Boils usually much below B.P. given on account of contained water. Heated with solid $KHSO_4$ gives acrolein, which possesses a pungent odour and is lachrymatory.	B.P. 258	M.P. 76

THE IDENTIFICATION OF HYDROCARBONS AND ETHERS

296. General Remarks.—In this section are included hydrocarbons, ethers, and similar unreactive compounds of C and H, or C, H, and O, that have not been included in the previous sections.

Usually, if the compound under examination does not dissolve in fuming sulphuric acid, nor react with nitric acid or fuming nitric acid, it is aliphatic in nature. Care must be exercised in testing with nitric acid since the phenolic ethers are nitrated with explosive violence.

Substances should be tested with bromine dissolved in dry carbon tetrachloride or chloroform. Decolorisation without the evolution of hydrobromic acid denotes unsaturation, but when accompanied by the copious disengagement of hydrogen bromide the reaction denotes substitution.

Since there is no simple qualitative test known for the detection of oxygen present in an organic compound, both the hydrocarbons and the relatively inert oxygen derivatives are grouped together in the following tables :—

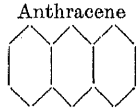
297. Properties of Solid Hydrocarbons and Ethers containing C.H.[O] only.

M.P. °C.	B.P. °C.	Name.	Characteristics.
22	233	Anethole $CH:CH.CH_3$  OCH_3	Odour of aniseed. $\Delta = 0{\cdot}986$ (22°). v.s.s. water; miscible with alcohol, ether. Oxidised with dilute HNO_3 gives anisaldehyde. With conc. H_2SO_4 gives anisoïn, $(C_{10}H_{12}O)_n$, which crystallises in small needles from ether, M.P. 140°.
26	261	Diphenylmethane $CH_2(C_6H_5)_2$	$\Delta = 1{\cdot}001$ (26°). Odour of oranges. With CrO_3 dissolved in H_2SO_4 gives benzophenone, M.P. 48°, B.P. 306°.

Properties of Solid Hydrocarbons and Ethers—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
28	252	Diphenyl Ether $C_6H_5.O.C_6H_5$	Odour of geraniums. Long needles. i.s. water; e.s. alcohol. Very stable. Dissolved in fuming HNO_3 gives dinitro-compound, M.P. 135°.
37	274	Ethyl-β-Naphthyl Ether β-$C_{10}H_7.O.C_2H_5$	Odour of aniseed. Crystalline mass. Heated with $AlCl_3$ gives β-Naphthol.
51	159	Camphene $C_{10}H_{16}$	Optically active. Forms feathery crystals. i.s. water; s. alcohol. Is the only natural solid terpene. $\Delta = 0{\cdot}842$ (54°). With Br dissolved in CCl_4 forms dibromide, M.P. 89°. Dry HCl gas in alcoholic solution precipitates the hydrochloride, M.P. 149°.
70	254	Diphenyl $C_6H_5.C_6H_5$	$\Delta = 1{\cdot}165$. i.s. water; s. alcohol. With Br dissolved in CS_2 forms *p*-brom-derivative, B.P. 310°, and in presence of iron forms *pp*-dibrom-compound, M.P. 169°. Oxidised with CrO_3 in acetic acid, benzoic acid is formed, M.P. 121°.
72	274	Methyl-β-Naphthyl Ether β-$C_{10}.H_7.O.CH_3$	Neroline. Odour of orange blossoms. s.s. alcohol. Heated with $AlCl_3$ forms β-Naphthol.
80	218	Naphthalene $C_{10}H_8$	Characteristic odour. $\Delta = 1{\cdot}152$ (15°). i.s. water; e.s. alcohol. With Br dissolved in CCl_4 substitution takes place easily. Picrate is precipitated from absolute alcohol solution, M.P. 150°. Nitrated at the ordinary temperature with HNO_3 and conc. H_2SO_4 forms α-nitro-naphthalene, M.P. 61°, after recrystallisation.
92	358	Triphenylmethane $CH(C_6H_5)_3$	Leaflets. i.s. water; s. alcohol, ether. Nitrated in the cold with excess of fuming HNO_3 gives trinitro-derivative, M.P. 206°. This solid dissolved in glacial acetic acid, and reduced with Zn dust in hot solution until the colour is almost discharged, gives on addition of PbO_2 an intense magenta solution.

Properties of Solid Hydrocarbons and Ethers—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
100	340	Phenanthrene 	Sublimes. m.s. alcohol; e.s. ether. Solutions fluorescent. Picrate precipitates from alcoholic solution on cooling, M.P. 143°, forms yellow needles after recrystallisation.
112	295	Fluorene  CH_2	Leaflets, violet fluorescence. s.s. alcohol. Picrate formed in ethereal solution, reddish brown, unstable, M.P. 80°. Oxidised by CrO_3 in glacial acetic acid gives fluorenone $(C_6H_4)_2CO$, M.P. 84°, B.P. 341°. Nitrated in glacial acetic acid gives 2-nitro-derivative, M.P. 153°.
216	351	Anthracene 	Usually somewhat yellow; violet fluorescence. s.s. alcohol, ether; e.s. benzene. Picrate formed in benzene solution, deep red, s. benzene, M.P. 138°. Oxidised by CrO_3 in glacial acetic acid to anthraquinone, M.P. 275°, which is identified by test given on page 170.

298. Properties of Liquid Hydrocarbons and Ethers containing C.H.[O] only.

B.P. °C.	Δ 0°C.	Name.	Characteristics.
35	0·719 (15°)	Diethyl Ether $C_2H_5.O.C_2H_5$	Characteristic odour. s.s. water; miscible with alcohol.
36	0·691	Isoprene $CH_2 : CH.C.CH_3 : CH_2$	Unsaturated. Unstable. Treated with conc. HCl or acetic anhydride and then steam distilled, forms a rubber-like mass.
37	0·634 (15°)	Pentane C_5H_{12}	Constituent of light petroleum ether.
69	0·677	Hexane C_6H_{14}	Constituent of petroleum ether.

Properties of Liquid Hydrocarbons and Ethers—*continued.*

B.P. °C.	Δ 0°C.	Name.	Characteristics.
80	0·874 (20°)	Benzene C_6H_6	M.P. 5·4°. Readily brominated and sulphonated. Nitrated with H_2SO_4 and HNO_3, or fuming HNO_3, gives *m*-dinitrobenzene, M.P. 89°.
81	0·790 (20°)	Cyclo-hexane C_6H_{12}	M.P. 4·7°. Not easily nitrated or brominated.
98	0·689 (15°)	Heptane C_7H_{14}	Cannot be nitrated or sulphonated.
111	0·878	Toluene $C_6H_5.CH_3$	Readily nitrated and sulphonated. Nitrated with fuming HNO_3 and fuming H_2SO_4 at ordinary temperatures gives 2 : 4 dinitro-derivative, M.P. 70°, after recrystallisation. Trinitro-toluene, obtained at 150° C., M.P. 80°.
136	0·883	Ethyl Benzene $C_6H_5.C_2H_5$	Oxidised with alkaline $KMnO_4$ + V_2O_5 gives benzoic acid, M.P. 121°. Trinitro-derivative M.P. 37°.
138	0·880	*p*-Xylene *p*-$C_6H_4.(CH_3)_2$	M.P. 15°. Insoluble in cold H_2SO_4. Nitrated at 10° C. with fuming HNO_3 gives 2-nitro-*p*-xylene, B.P. 239°. Boiled 1 minute with 2 parts of H_2SO_4 and 1 part of fuming HNO_3 gives trinitro-derivative, M.P. 138°, after recrystallisation. Oxidised with alkaline $KMnO_4$ gives terephthalic acid.
139	0·880	*m*-Xylene *m*-$C_6H_4(CH_3)_2$	Soluble in cold H_2SO_4. Nitrated as described for the *p*-isomer, gives trinitro-derivative, M.P. 181°. Oxidation with alkaline $KMnO_4$ gives isophthalic acid, which sublimes at 300° C.
142	0·893	*o*-Xylene *o*-$C_6H_4(CH_3)_2$	Soluble in H_2SO_4. Nitro-derivative obtained by procedure given for *p*-isomer, is an oil. Oxidation with alkaline $KMnO_4$ gives phthalic acid, M.P. 184° *d*.

Properties of Liquid Hydrocarbons and Ethers—*continued.*

B.P. °C.	Δ 0°C.	Name.	Characteristics.
153	0·878	Cumene $C_6H_5.CH(CH_3)_2$	Oxidation with alkaline $KMnO_4$ and V_2O_5 gives benzoic acid, M.P. 121°.
155	0·988 (21°)	Anisole $C_6H_5.O.CH_3$	Aromatic odour. i.s. water; s. alcohol. Nitrated very readily; *o*-nitro-anisole, B.P. 265°; *p*-isomer, solid, M.P. 54°, can be separated by Buchner funnel and recrystallised. Warmed with $AlCl_3$ or heated with conc. HI to boiling, gives phenol.
156	0·860 (20°)	Pinene $C_{10}H_{16}$	Principal constituent of turpentine. Unsaturated. Optically active (*d* or *l*). Reacts with violence with fuming HNO_3. Well cooled and treated with *dry* HCl gas forms hydrochloride, M.P. 125°, odour of camphor. Dibromide, M.P. 164°.
164	0·877 (4°)	Mesitylene $2:4:6\text{-}C_6H_3(CH_3)_3$	Nitrated as directed for *p*-xylene gives trinitro-derivative, M.P. 235°. Nitrated with 1 part HNO_3 and 1 part H_2O at 50° gives mononitro-derivative, M.P. 41°.
171	0·856 (10°)	Phellandrene $C_{10}H_{16}$	Occurs in fennel oil. i.s. water, alcohol; s. ether. Dextro-rotatory.
172	0·982	Phenetole $C_6H_5.O.C_2H_5$	Aromatic odour. i.s. water; s. alcohol. Heated with $AlCl_3$ or conc. HI gives phenol. Nitrated and separated as described in anisole, gives ortho-derivative, B.P. 267° and para-, M.P. 58°.
175	0·872	Cymene $p\text{-}CH_3.C_6H_4.CH(CH_3)_2$	Oxidised by alkaline $KMnO_4$ and V_2O_5 to terephthalic acid, which sublimes above 300°.
176	0·927 (20°)	Cineol $C_{10}H_{18}O$	Agreeable camphor-like odour. Unsaturated. Hydrochloride is precipitated if dissolved in dry ligroin and dry HCl gas passed through.

Properties of Liquid Hydrocarbons and Ethers—*continued.*

B.P. °C.	Δ 0°C.	Name.	Characteristics.
176	0·853 (10°)	Limonene $C_{10}H_{16}$	Occurs in oil of lemon. Optically active *d* or *l*. $[\alpha]_D = \pm 106°$. Resembles pinene. Dissolved in glacial acetic acid and Br added, tetrabromide is precipitated, M.P. 104°.
176	0·851 (16°)	Sylvestrene $C_{10}H_{16}$	Occurs in Russian turpentine. Optically active, $[\alpha]_D = +66·3$. Tetrabromide, prepared as described for limonene, M.P. 135°. Dihydrochloride, M.P. 72°, precipitated by dry HCl gas. Dissolved in acetic anhydride and 1 drop H_2SO_4 added, an intense blue coloration is given.
205	1·086 (15°)	Veratrole o-$C_6H_4(OCH_3)_2$	M.P. 15°. Heated with conc. HI or $AlCl_3$ catechol is formed. Fuming HNO_3 gives nitro-compound, M.P. 95°. Dibromide, M.P. 91°.
233	0·986 (22°)	Anethole	See page 177 (M.P. 22°).
252		Diphenyl Ether $C_6H_5.O.C_6H_5$	See page 178 (M.P. 28°).
269	1·096 (14°)	Methyl α-Naphthyl Ether α-$CH_3.O.C_{10}H_7$	Heated with conc. HI or with $AlCl_3$ gives α-naphthol. Forms red crystalline picrate.

SCHEME OF ANALYSIS OF COMPOUNDS CONTAINING HALOGEN. [C.H.[O] AND HALOGEN]

300. General Remarks.—Compounds of this class are usually colourless. They give either an acid or neutral reaction with litmus, but not an alkaline reaction. In general the substitution of a hydrogen atom in an organic substance by halogen does not greatly modify the general characteristics of the compound. Thus solubility is not greatly affected, *e.g.*, the chlorhydrocarbons and chlorethers are insoluble; the halogen-substituted fatty acids are generally soluble in cold water. In the same way the reactivity of the remainder of the molecule is not usually appreciably altered, *e.g.*, the nitration of chlorbenzene and of benzene are effected under similar conditions. The specific gravity is, however, invariably greater.

TABLE V

301. General Table of Analysis of Halogen Compounds.

Odour.

Irritating, frequently lachrymatory:	halogen-substituted ketones; aromatic compounds, halogen-substituted in the side chain.
Sweetish odour:	halogen-substituted aliphatic hydrocarbons, etc.

Solubility.

In general, solubility corresponds to that of parent substance (see Table II., page 132). Acid halides react readily with water with the formation of the free halogen acid.

Boil with Normal NaOH Solution.

If the substance is soluble in water, aqueous NaOH should be used. If insoluble, use alcoholic NaOH. Acidify with HNO_3 and add $AgNO_3$.
A precipitate of silver halide is produced readily in the case of most aliphatic halogen compounds, and in aromatic compounds substituted in the side chain, but is not usually produced in the case of aromatic compounds containing the halogen in the nucleus. It should be noted that usually iodine is more easily displaced than bromine; and bromine than chlorine.

Boil with Aqueous or Alcoholic $AgNO_3$ slightly acidified with HNO_3.

The rate of formation of a precipitate of silver halide indicates the ease with which the halogen may be replaced and thus supplements the previous test.

Examine the Compound by the Generic Tests given on page 132 in order to determine its nature.

NOTE.—A few halogen compounds react so readily with alkali, owing to the ease of replacement of the halogen atom, that they appear to be acidic in nature when not truly so.

Identify the Compound by the following Tables.

302. The Properties of Solid Substances containing C.H.[O].Cl only.

M.P. °C.	B.P. °C.	Name.	Characteristics.
28	214	*m*-Chlorphenol m-C_6H_4.(OH).Cl	White crystals. Acid reaction to litmus. Fusion with alkalies gives resorcinol.
37	217	*p*-Chlorphenol p-C_6H_4.(OH).Cl	White crystals. Faint unpleasant odour. v.s.s. water; e.s. alcohol. $\Delta = 1{\cdot}306$ (20°). Acid reaction to litmus. Fusion with alkalies gives resorcinol. Benzoyl derivative, M.P. 93°.
53	174	*p*-Dichlorbenzene p-$C_6H_4Cl_2$	White leaflets that easily sublime; e.s. alcohol, ether. Mono-nitro-derivative, M.P. 55°.
55	195	Trichloracetic Acid $CCl_3.COOH$	Deliquescent crystals; v.s. water, alcohol, ether. Strongly acid in reaction. Boiled with water and a little alkali gives $CHCl_3$. Methyl ester, B.P. 152°. Ethyl ester P.B. 167°.
56	265	β-Chlornaphthalene β-$C_{10}H_7Cl$	Colourless crystals. Halogen not easily replaced. $\Delta = 1{\cdot}266$ (16°).
57	97	Chloral Hydrate $CCl_3.CH(OH)_2$	Colourless tablets, penetrating odour. Neutral. s. water, alcohol, ether. M.P. affected by rate of heating. With conc. H_2SO_4 gives chloral, B.P. 98°. Odour of carbylamine when heated with NaOH and aniline. Aqueous solution gives yellow precipitate on standing with yellow $(NH_4)_2S_2$ solution.
58	244	ω-Chloracetophenone $C_6H_5.CO.CH_2Cl$	White tablets. Pungent odour, lachrymatory. i.s. water; e.s. alcohol, ether. $\Delta = 1{\cdot}324$ (15°). Halogen easily displaced.
62	189	Chloracetic Acid $CH_2Cl.COOH$	Deliquescent needles. Sharp odour. v.s. water, endothermic solution. Strongly acid in reaction. Methyl ester, B.P. 129°. Ethyl ester, B.P. 144°.
67	244	Trichlorphenol 2-4-6.$C_6H_2(Cl_3)$.OH	White needles; almost i.s. water; v.s. alcohol, ether. Strongly acid in reaction. Benzoyl derivative, M.P. 70°. Basalt precipitated. Titrates as a monobasic acid.

The Properties of Solid Substances—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
97	167	Trichlor-tert-butyl-alcohol "Chloretone" $(CH_3)_2.C(OH).CCl_3+1\frac{1}{2}H_2O$	White crystals, odour of camphor; s.s. hot water; v.s. alcohol, ether. Rotates vigorously when thrown on to water. Sublimes easily; steam volatile. Reduces ammoniacal $AgNO_3$. Boiled with alkalies gives acetone.
140	—	*o*-Chlorbenzoic Acid *o*-$C_6H_4.Cl.COOH$	White needles; e.s. hot water, alcohol, ether. Melts under water. Methyl ester, B.P. 234°. Ethyl ester, B.P. 243°.
153	—	*m*-Chlorbenzoic Acid *m*-$Cl.C_6H_4.COOH$	Crystallises in prisms; e.s. hot water, etc. Methyl ester, B.P. 231°. Ethyl ester, B.P. 245°.
182	—	Tetrachlornaphthalene 1-2-3-4 $C_{10}H_8Cl_4$	Large crystals; s.s. alcohol; e.s. ether. Rapidly heated gives HCl and 1 : 4 dichlornaphthalene, M.P. 67°.
226	326	Hexachlorbenzene C_6Cl_6	Crystallises in fine needles, almost i.s. water, alcohol; s.s. ether, benzene.
236	—	*p*-Chlorbenzoic Acid *p*-$Cl.C_6H_4.COOH$	White crystals, almost i.s. water; e.s. alcohol, ether. Methyl ester, M.P. 43°. Ethyl ester, B.P. 238°.

303. The Properties of Liquid Substances containing C.H.[O].Cl only.

B.P. °C.	Δ	Name.	Characteristics.
52	1·105 (20°)	Acetyl Chloride $CH_3.COCl$	Pungent odour. Fumes in air. Decomposed immediately by cold water. Anilide, M.P. 113°. *p*-Toluidide, M.P. 153°.
61	1·526 (0°)	Chloroform $CHCl_3$	Sweet odour. s.s. water; miscible with alcohol, ether. Non-combustible. Warmed with alcoholic KOH and aniline gives odour of carbylamine. Warmed with resorcinol and aqueous NaOH gives red fluorescent solution. Reduces Fehling's solution on heating.

The Properties of Liquid Substances—*continued.*

B.P. °C.	Δ	Name.	Characteristics.
71	1·236 (15°)	Methyl Chloroformate $Cl.COOCH_3$	Lachrymatory. Decomposed by cold water.
77	1·595 (20°)	Carbon Tetrachloride CCl_4	Sweetish odour. Almost i.s. water; miscible with ether, alcohol. Non-combustible. Gives the carbylamine reaction with difficulty.
79	1·065 (20°)	Propionyl Chloride $C_2H_5.COCl$	Pungent odour, resembling acetyl chloride. Fumes in air. Decomposed by cold water. Anilide, M.P. 104°. *p*-Toluidide, M.P. 124°.
83	1·252 (4°)	Ethylene Chloride CH_2Cl | CH_2Cl	Odour like chloroform, but does not reduce Fehling's solution.
94	1·135 (20°)	Ethyl Chloroformate $Cl.COOC_2H_5$	Lachrymatory. Resembles methyl ester. Decomposed by cold water.
98	1·512 (20°)	Chloral $CCl_3.CHO$	Oily liquid with penetrating odour. Reacts with water to give chloral hydrate, M.P. 57° (see page 184). Warmed with alkali gives $CHCl_3$. Reduces ammoniacal $AgNO_3$ on warming. Forms NH_3 compound, also bisulphite derivative.
105	1·495 (0°)	Chloracetyl Chloride $Cl.CH_2.COCl$	Pungent odour. Fumes in air. Decomposed by water giving monochloracetic acid (see page 184).
118	1·160 (15°)	Chloracetone $CH_3.CO.CH_2Cl$	Irritating odour. Lachrymatory. s.s. water; miscible with alcohol, ether. Forms bisulphite compound. Gives red colour with excess of KOH or of K_2CO_3. Reduced with Zn and acid gives acetone.
132	1·113 (15°)	Chlorbenzene C_6H_5Cl	Aromatic odour. Almost i.s. water. Halogen is not displaced with alcoholic potash. Nitrated with fuming HNO_3 in the cold and poured into water gives para-nitro-compound, which after recrystallisation, has M.P. 83°.

The Properties of Liquid Substances—*continued.*

B.P. °C.	Δ	Name.	Characteristics.
145	1·158 (20°)	Ethyl Chloracetate $Cl.CH_2.COOC_2H_5$	Pleasant odour.
158	1·081 (20°)	*o*-Chlortoluene *o*-$Cl.C_6H_4.CH_3$	Almost i.s. water. Halogen is not displaced with alcoholic potash. Alkaline $KMnO_4$ gives *o*-chlorbenzoic acid, M.P. 140°. On nitration with H_2SO_4 and HNO_3 at 30° gives 1 : 2 : 5 derivative, M.P. 44°.
162	1·070 (20°)	*p*-Chlortoluene *p*-$Cl.C_6H_4.CH_3$	Resembles ortho-isomeride above. *p*-Chlorbenzoic acid, M.P. 236°. Nitro-derivative, M.P. 38°.
175	1·30	*o*-Chlorphenol *o*-$Cl.C_6H_4.OH$	M.P. 7°. Unpleasant odour. Halogen is not readily displaced, but fusion with KOH gives resorcinol. Benzoyl derivative, M.P. 213°.
179	1·327 (0°)	*o*-Dichlorbenzene *o*-$C_6H_4.Cl_2$	Almost i.s. water.
179	1·104 (15°)	Benzyl Chloride $C_6H_5.CH_2Cl$	Sharp odour. Lachrymatory. Boiled with K_2CO_3 solution gives benzyl alcohol, B.P. 205°. Oxidised by alkaline $KMnO_4$ to benzoic acid, M.P. 121°.
193	1·570 (15°)	Dichloracetic Acid $CHCl_2.COOH$	Soluble in water. Strongly acid in reaction. Methyl ester, B.P. 143°. Ethyl ester, B.P. 157°.
197	1·219 (15°)	Benzoyl Chloride $C_6H_5.COCl$	Sharp odour. Lachrymatory. Slowly decomposed by water. Hydrolysis gives benzoic acid, M.P. 121°. Anilide, M.P. 160°. *p*-Toluidide, M.P. 158°.
204	1·270 (0°)	Benzal Chloride $C_6H_5.CHCl_2$	Sharp odour. Boiled with Na_2CO_3 solution gives benzaldehyde. Alkaline $KMnO_4$ gives benzoic acid, M.P. 121°.
213	1·380 (14°)	Benzo-trichloride $C_6H_5.CCl_3$	Pungent odour. Saponified by alkalies giving benzoic acid, M.P. 121°. Boiled with absolute alcohol gives ethyl benzoate, B.P. 213°.
263	1·194 (20°)	α-Chlornaphthalene α-$C_{10}H_7Cl$	Readily forms a yellow picrate, M.P. 137°.

304. The Properties of Solid Compounds containing C.H.[O].Br only.

M.P. °C.	B.P. °C.	Name.	Characteristics.
28	185	*p*-Bromtoluene $p\text{-Br.C}_6\text{H}_4\text{CH}_3$.	Very stable towards alkalies. Oxidised with alkaline $KMnO_4$ gives *p*-brombenzoic acid, M.P. 251°.
32	236	*m*-Bromphenol $m\text{-Br.C}_6\text{H}_4\text{.OH}$	Unpleasant odour. Fusion with solid KOH gives chiefly resorcinol.
48	—	Dibromacetic Acid $CHBr_2.COOH$	Soluble in water. Strongly acid in reaction. Deliquescent. Ag salt on boiling with water precipitates AgBr. Ethyl ester, B.P. 192°.
50	—	ω-Bromacetophenone $C_6H_5.CO.CH_2Br$	Crystallises in prisms. Extremely lachrymatory. Almost i.s. water; e.s. alcohol ether. Slowly neutrali sed by alkali.
50	208	Bromacetic Acid $CH_2Br.COOH$	Sharp smell. Soluble in water. Strongly acid in reaction. Pb salt soluble in hot water. Ag salt precipitated; explodes on heating. Ethyl ester, lachrymatory, B.P. 169°.
53	—	Bromal Hydrate $CBr_3.CH(OH)_2$	Soluble in water. On distillation gives bromal (B.P. 174°), see page 189.
63	235	*p*-Bromphenol $p\text{-Br.C}_6\text{H}_4\text{.OH}$	e.s. alcohol, ether. Fusion with KOH gives resorcinol.
76	274	*a*-Bromcamphor $C_8H_{14}\begin{cases}\text{CHBr}\\ \text{CO}\end{cases}$	Odour of camphor; i.s. water. Optically active. With NH_2OH gives camphoroxime M.P. 120°.
93	190	Carbon Tetrabromide CBr_4	Ethereal odour. Sublimes. Easily decomposed by alcoholic KOH. Compare CCl_4, page 186.
96	—	Tribromphenol $2{:}4{:}6\text{-Br}_3\text{.C}_6\text{H}_2\text{.OH}$	Crystallises in fine needles. Easily sublimed. Almost i.s. cold water; v.s. alcohol. Strongly acid in reaction. Benzoyl derivative, M.P. 81°.

The Properties of Solid Compounds—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
131	—	Tribromacetic Acid $CBr_3.COOH$	e.s. water, alcohol. Strongly acid in reaction. Solutions of the acid and salts decompose on heating. Ag salt precipitated.
148	—	*o*-Brombenzoic Acid *o*-$Br.C_6H_4.COOH$	e.s. hot water, alcohol. Ba salt very soluble. Methyl ester, B.P. 242°. Ethyl ester, B.P. 254°.
155	280	*m*-Brombenzoic Acid *m*-$Br.C_6H_4.COOH$	s.s. water; e.s. alcohol, ether. Methyl ester, M.P. 31°. Ethyl ester, B.P. 259°.
251	—	*p*-Brombenzoic Acid *p*-$Br.C_6H_4.COOH$	s.s. hot water; e.s. alcohol, ether. Methyl ester, M.P. 74°. Ethyl ester, B.P. 262°.

305. The Properties of Liquid Compounds containing C.H.[O].Br only.

B.P. °C.	Δ	Name.	Characteristics.
38	1·450 (15°)	Ethyl Bromide C_2H_5Br	Ethereal odour. Almost i.s. water, miscible with alcohol. Reacts with hot alcoholic $AgNO_3$. C_2H_4 evolved with alcoholic KOH.
131	2·182 (20°)	Ethylene Bromide CH_2Br | CH_2Br	Sweetish odour. Almost i.s. water; miscible with alcohol. M.P. 8° C. Reacts readily with excess of alcoholic KOH, yielding acetylene.
156	1·499 (15°)	Brom-benzene C_6H_5Br	Almost i.s. water. Very stable towards alkalies. When nitrated with $HNO_3 + H_2SO_4$, poured into water, and the product extracted with *small* quantities of alcohol, gives a residue of para-nitro-compound which on recrystallisation has M.P. 126°.
174	3·34	Bromal $CBr_3.CHO$	Compare Chloral (page 186). Reacts with water to give crystalline hydrate, M.P. 53°. Decomposed by aqueous KOH yielding a formate. Forms a bisulphite-compound.

The Properties of Liquid Compounds—*continued.*

B.P. °C.	Δ	Name.	Characteristics.
180	1·431 (15°)	*o*-Bromtoluene *o*-$CH_3.C_6H_4.Br$	Very stable. Oxidised by alkaline $KMnO_4$ to to the corresponding acid, M.P. 148°.
184	1·201	*m*-Bromtoluene *m*-$CH_3.C_6H_4.Br$	Oxidised by alkaline $KMnO_4$ to the corresponding acid, M.P. 155°.
193	—	*o*-Bromphenol *o*-$Br.C_6H_4.OH$	Unpleasant odour. Almost i.s. water; miscible with alcohol. Fusion with KOH gives resorcinol.

306. The Properties of Solid Compounds containing C.H.[O].I only.

M.P. °C.	B.P. °C.	Name.	Characteristics.
35	211	*p*-Iodotoluene *p*-$CH_3.C_6H_4I$	Almost i.s. water. Oxidised by alkaline $KMnO_4$ to *p*-iodobenzoic acid, M.P. 265°. Chlorine passed through chloroform solution gives dichloride $CH_3C_6H_2.ICl_2$, M.P. 85° *d*.
119	dec.	Iodoform CHI_3	Forms lemon-yellow hexagonal plates. Characteristic and persistent odour. Almost i.s. water; m.s. alcohol; e.s. ether, chloroform. Easily sublimes. Steam-volatile. If a small quantity is warmed with a little phenol dissolved in dilute alcoholic KOH, a red colour is formed. Gives carbylamine reaction with aniline and alcoholic KOH.
210*d*	—	Iodosobenzene C_6H_5IO	Amorphous. s.s. water, alcohol; i.s. ether. Liberates iodine from KI. Decomposed slowly by boiling water to $C_6H_5IO_2$ and C_6H_5I. Crystallises from glacial acetic acid as acetate, M.P. 156°.
227*d*	—	"Iodoxybenzene" $C_6H_5IO_2$	Crystallises in long needles. s. hot water. Liberates iodine from KI and Cl_2 from conc. HCl.

307. The Properties of Liquid Compounds containing C.H.[O].I only.

B.P. °C.	Δ	Name.	Characteristics.
42·5	2·285 (15°)	Methyl Iodide CH_3I	Sweet-smelling liquid. Often contains free iodine. Almost i.s. water; miscible with alcohol, ether. Precipitate of AgI, in the cold, with alcoholic $AgNO_3$.
72	1·943 (15°)	Ethyl Iodide C_2H_5I	Resembles CH_3I (above). Heated with alcoholic KOH, ethylene is evolved.
89	1·703 (20°)	Isopropyl Iodide $(CH_3)_2.CHI$	Resembles CH_3I (above). Decomposed by boiling water.
102	1·743 (20°)	Propyl Iodide $C_2H_5.CH_2I$	Resembles CH_3I (above).
102	1·830 (20°)	Allyl Iodide $CH_2 : CH.CH_2I$	Resembles CH_3I (above). Odour of leeks. By continued shaking of the alcoholic solution with mercury, C_3H_5HgI separates in colourless leaflets, M.P. 135°.
188	1·840 (15°)	Phenyl Iodide $C_6H_5.I$	Does not usually contain free iodine, and is quite stable towards alcoholic $AgNO_3$. In ice cold $CHCl_3$ solution, dry chlorine precipitates $C_6H_5ICl_2$, in yellow needles, which decomposes above 80° C.
204	1·697 (20°)	*o*-Iodotoluene *o*-$CH_3.C_6H_4.I$	Resembles phenyl iodide (above). Dichloride, M.P. 91° *d*. Oxidation with dilute HNO_3 gives *o*-iodobenzoic acid, M.P. 162°.
204	1·698 (20°)	*m*-Iodotoluene *m*-$CH_3.C_6H_4.I$	Oxidation with dilute HNO_3 gives *m*-Iodobenzoic acid, M.P. 186°.

THE IDENTIFICATION OF COMPOUNDS CONTAINING C.H.[O].S ONLY

308. The more important sulphur-containing compounds belong to one of the following classes :—

(*a*) **Mercaptans and Thiophenols R.SH,** which usually

(i.) possess an unpleasant odour (garlic);
(ii.) are insoluble in water; but
(iii.) are soluble in caustic alkali solutions;
(iv.) form well-crystallised mercuric mercaptides, of definite M.P., and lead mercaptides of a yellow colour;
(v.) are easily oxidised by nitric acid or $KMnO_4$ to sulphonic acids.

(*b*) **Thioethers and Sulphides, R.S.R,** which usually

(i.) possess a powerful garlic odour;
(ii.) are insoluble in water *and* alkali;
(iii.) are oxidised by HNO_3 or $KMnO_4$ to sulphones;
(iv.) and often give addition products with the halogens, alkyl iodides and with mercuric chloride.

(*c*) **Sulphoxides, R.SO.R,** which usually

(i.) are odourless and neutral;
(ii.) are oxidised to sulphones by HNO_3 or $KMnO_4$.

(*d*) **Sulphones, $R.SO_2.R$,** which usually

(i.) are odourless and neutral;
(ii.) are very stable and not attacked by oxidising agents.

(*e*) **Sulphonic Acids, and esters of sulphonic, sulphuric and sulphurous acids,** which usually

are acid, or faintly acid in reaction.

(*f*) **Thiophene Compounds,** which

give intense blue colorations with isatine and sulphuric acid.

It should be remembered that it may be necessary to identify organic sulphur compounds, which also contain a simple metal, particularly as in commerce the sulphonic acids are usually isolated in the form of their salts, since frequently the acids are deliquescent and cannot be extracted by ether from their aqueous solutions. The sodium bisulphite compounds of aldehydes and ketones are occasionally, but not often, met with. In this case the aldehyde, or ketone, is readily obtained by the action of acid or alkali, and sulphur dioxide is evolved on acidification.

Sulphonic acids and metallic sulphonates may be identified by the determination of their equivalent weight by titration, or by estimation of the percentage of metal in the anhydrous salt, and also by the conversion to the acid chloride and amide by the following method. Warm the anhydrous acid or salt with phosphorus pentachloride, wash the cooled product with cold water to remove excess of the reagent. If the product is solid, recrystallise a little from ether or chloroform, and take the M.P. Convert the bulk of the acid chloride to the sulphon-amide by evaporation with strong ammonia and recrystallisation, or to the methyl or ethyl ester by refluxing with the absolute alcohol and 3 per cent. of dry hydrogen chloride (see page 73).

309. Scheme of Analysis of Compounds containing C.H.[O].S only.

TABLE VI

Solubility.	Soluble, and acid in reaction. Sparingly soluble and faintly acid in reaction. Relatively insoluble and practically neutral in reaction.	Sulphonic and sulphinic acids, etc. Alkyl sulphates, sulphites, etc. Sulphones, mercaptans, thiophenols, sulphides, disulphides, etc.
Odour.	Powerful garlic, or unpleasant odour.	Mercaptans, thiophenols, sulphides, disulphides, etc.
Warm with Dilute NaOH solution.	Soluble, but relatively insoluble in *water*.	(*a*) Mercaptans, thiophenols. (*b*) Alkyl sulphites, sulphates, etc., with decomposition.
Fuse for 5 minutes with moistened NaOH or KOH, cool, dissolve in water. Acidify with H_2SO_4. Test the gases evolved with lead acetate paper, and then with dilute $KMnO_4$ solution.	H_2S evolved. SO_2 evolved.	Mercaptans, thiophenols, sulphides, disulphides (*i.e.*, those containing divalent sulphur). Sulphonic and sulphinic compounds, sulphones, sulphoxides, etc.
Treat with dilute acid $KMnO_4$ solution.	Readily oxidised.	Mercaptans, thiophenols, sulphides, sulphoxides.
Treat with aqueous or alcoholic $FeCl_3$.	Fugitive "phenolic" reaction.	Probably phenolic sulphonic acids or their derivatives.
Warm with aqueous or alcoholic solutions of mercuric chloride, or of lead acetate.	Mercuric (colourless) or lead (yellow) salts produced. The mercuric compounds should be recrystallised from alcohol, and their M.P. determined.	Mercaptans, thiophenols, and some sulphides.

If solid, identify by table on page 194; if liquid, by table on page 196.

310. The Properties of Solid Compounds containing C.H.[O].S only.

M.P. °C.	B.P. °C.	Name.	Characteristics.
43	—	Benzene Sulphonic Acid (Hydrate)	See anhydrous acid (M.P. 65°).
65	—	Benzene Sulphonic Acid $C_6H_5.SO_3H$	v.s. water, alcohol; i.s. ether. Strongly acid in reaction. Chloride, M.P. 15°, B.P. 246° *d*. Yields amide, M.P. 150°, and *p*-toluidide, M.P. 121°.
70	340 *d*.	Diphenyl Sulphoxide $(C_6H_5)_2.SO_2$	e.s. alcohol, ether. Oxidised by acetic acid solution of $KMnO_4$ to diphenyl sulphone, M.P. 128°. Reduced by Zn and acid to diphenyl sulphide, B.P. 296°.
76	—	Trional $CH_3 > C(SO_2C_2H_5)_2$ C_2H_5	Lustrous scales. s.s. cold water; s. alcohol, ether. Neutral. In its reactions it resembles sulphonal, M.P. 125°.
83	*d*.100°	Benzene Sulphinic Acid $C_6H_5.SO_2H$	Strongly acid. e.s. hot water, alcohol, ether. Readily oxidised to benzene sulphonic acid. Alkali fusion gives C_6H_6 and Na_2SO_3.
85	—	Tetronal $(C_2H_5)_2.C.(SO_2C_2H_5)_2$	Lustrous tablets. Resembles trional (M.P. 76°) and sulphonal (M.P. 125°).
85-90	—	α-Naphthalene Sulphonic Acid α-$C_{10}H_7.SO_3H + H_2O$	Deliquescent. e.s. water; s. alcohol; d.s. ether. Strongly acid in reaction. Ba salt sparingly soluble. Methyl ester, M.P. 78°. Chloride, M.P. 67°. Amide, M.P. 150°.
92	—	*p*-Toluene Sulphonic Acid *p*-$CH_3.C_6H_4.SO_3H$	e.s. water. Strongly acid reaction Chloride, M.P. 69°. Amide, M.P. 137°. Alkali fusion gives *p*-cresol and *p*-oxybenzoic acid. Ba salt sparingly soluble.

The Properties of Solid Compounds—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
106	—	1-Naphthol-8-Sulphonic Acid $HO.C_{10}H_6.SO_3H + H_2O$	v.s. water. Strongly acid in reaction. $FeCl_3$ gives fugitive green colour. Pb salt precipitated.
122	—	2-Naphthol-6-Sulphonic Acid $HO.C_{10}H_6.SO_3H$	Schäffer's acid. Forms leaflets which redden on melting. e.s. water. $FeCl_3$ gives pale green colour. Ba salt easily soluble.
125	300° *d.*	Sulphonal $(CH_3)_2.C.(SO_2C_2H_5)_2$	Colourless, odourless. Neutral. Very stable. e.s. hot water and hot alcohol. e.s. conc. H_2SO_4 and precipitated unchanged on dilution. Heated with metallic Na gives unpleasant odour of mercaptan.
128	376°	Diphenyl Sulphone $(C_6H_5)_2.SO_2$	Very stable. s.s. hot water; s. alcohol, benzene. Alkaline fusion gives phenol. Does not give mercaptan odour on heating with Na (see Sulphonal, above).
154	360°	1-Naphthol-8-Sulphonic Acid Anhydride $C_{10}H_6.SO_2O$	Crystallises in prisms. s.s. alcohol; s. benzene. Dissolves slowly in hot conc. NaOH giving salt of acid described above (M.P. 106°).
170 *d.*	—	1-Naphthol-4-Sulphonic Acid $HO.C_{10}H_6.SO_3H$	Neville and Winther's Acid. e.s. water. Strongly acid in reaction. Sodium salt soluble in methylated spirit. $FeCl_3$ gives fugitive, intense blue colour.
193 *d.*	—	*d*-Camphor-β-Sulphonic Acid $SO_3H.C_8H_{13}\begin{matrix}CH_2\\ \vert \\ CO\end{matrix}$	e.s. water. Optically active. With SO_2Cl_2 gives chloride, M.P. 67°. Amide, M.P. 132°. Methyl ester. M.P. 61°.
—	—	β-Naphthalene Sulphonic Acid β-$C_{10}H_7.SO_3H$	s. in water. Not deliquescent. Oxidised with acid $KMnO_4$ solution gives phthalic acid. Chloride, M.P. 76°.

311. The Properties of Liquid Compounds containing C.H.[O].S only.

B.P. °C.	Δ	Name.	Characteristics.
36	0·839 (20°)	Ethyl Mercaptan $C_2H_5.SH$	Garlic odour. Almost i.s. water. Miscible with alcohol. Alcoholic $FeCl_3$ gives blue colour. Mercuric salt, M.P. 76°. Lead salt (yellow), M.P. 150°. Benzoyl derivative, B.P. 252°.
37	0·854 (20°)	Dimethyl Sulphide $(CH_3)_2.S$	Odour somewhat disagreeable. i.s. water. Oxidised by aqueous $KMnO_4$ gives dimethyl sulphone, M.P. 109°, B.P. 238°. HgI_2 compound, M.P. 67°.
46	1·263 (20°)	Carbon Disulphide CS_2	Unpleasant odour. i.s. water. Miscible with organic solvents. Very inflammable, blue flame. Dissolve one drop in alcoholic NaOH and add an equal volume of water, acidify with acetic acid and add one drop $CuSO_4$ solution. Voluminous yellow precipitate readily forms.
84	1·705 (15°)	Thiophene C_4H_4S	Faint odour. i.s. water. Violent action with HNO_3. Add a dilute solution in *pure* benzene to a solution of isatine in conc. H_2SO_4 containing a trace of $FeCl_3$ and shake, an intense blue colour appears.
92	0·836 (20°)	Diethyl Sulphide $(C_2H_5)S_2$	Disagreeable odour. i.s. water. $HgCl_2$ compound, obtained from alcoholic solution, M.P. 90°. Oxidised gives diethyl sulphone, M.P. 70°, B.P. 248°. HgI_2 compound, M.P. 110°.
121	1·048 (15°)	Dimethyl Sulphite $(CH_3)_2SO_3$	Pleasant odour. Ester of sulphurous acid. Easily saponified.
138	0·888 (27°)	Allyl Sulphide $(C_3H_5)_2S$	Odour of garlic. Almost i.s. water. $AgNO_3$ compound is precipitated from alcoholic solution.
158	1·100 (4°)	Diethyl Sulphite $(C_2H_5)_2SO_3$	Compare Methyl ester (B.P. 121°).

The Properties of Liquid Compounds—*continued.*

B.P. °C.	Δ	Name.	Characteristics.
169	1·078 (24°)	Thiophenol C_6H_5SH	Unpleasant odour. i.s. water. Solution in conc. H_2SO_4 turns red and finally blue on warming. Cu, Pb and Ag salts (yellow) precipitated from alcoholic solution. Benzoyl derivative, M.P. 56°.
188	1·333 (15°)	Dimethyl Sulphate $(CH_3)_2.SO_4$	Oily liquid. Almost i.s. water. Vapour very poisonous (see page 80). Ester of sulphuric acid. Easily hydrolysed.
199	1·024 (15°)	Allyl Disulphide $(C_3H_5)_2S_2$	Strong garlic odour. Almost i.s. water. Chief constituent of oil of garlic.
208	1·199 (0°)	Diethyl Sulphate $(C_2H_5)_2SO_4$	Peppermint odour. Very poisonous. Almost i.s. water. Easily hydrolysed. See Methyl ester (B.P. 188°), and page 80.
296	1·119 (15°)	Diphenyl Sulphide $(C_6H_5)_2S$	Odour of leeks. Almost i.s. water. Br yields dibrom-derivative, M.P. 109°. Easily oxidised to diphenyl sulphone, M.P. 128°.

SCHEME OF ANALYSIS OF COMPOUNDS CONTAINING C.H.[O].N ONLY

315. The analytical detection of nitrogenous compounds is more complicated than that of nitrogen-free substances, as it is often difficult to assign the compound to a definite class by the use of a series of generic tests.

TABLE VII

Preliminary Tests for Compounds containing C.H.[O].N

Colour.

All azo-compounds and dyes and the majority of azoxy-compounds have a pronounced colour. Nitro-compounds are generally yellow, and frequently the colour is intensified by the addition of alkali.

Solubility in cold dilute NaOH.

Substances that are relatively insoluble in water, but are soluble in cold dilute NaOH, are acidic in nature, and probably belong to one of the following classes :—

nitro-phenols (form coloured solutions with alkalies) ;
simple amides, imides, amino- and nitro-carboxylic acids ; oximes ; some purines.

N.B.—Ammonia is evolved in the cold from ammonium salts of organic acids and from aldehyde-ammonias.

Solubility in dilute HCl.

Substances that are relatively insoluble in water, but soluble in dilute acids, and usually reprecipitated by alkalies, probably belong to one of the following classes :—

amines ; hydrazines ; alkaloids ;

and in some cases,

oximes ; purines ; amides.

Treat the substances with a strong solution of NaOH, and warm.

Ammonia or ammoniacal vapours are evolved in the cold from ammonium salts, salts of aliphatic amines, aldehyde ammonias.
Ammonia or ammoniacal vapours are evolved on heating amides, imides, guanidines, nitriles (slowly), some nitro-anilines.
Liquid or solid bases are liberated from salts of amines, or from acyl derivatives of amines.

Heat the substance with soda-lime.

Ammonia or ammoniacal vapours are evolved from salts of aliphatic amines, amides, imides, nitriles, most alkaloids, purines, hydrazines, simple amino-acids, many nitro-anilines.

316. SCHEME OF ANALYSIS OF SIMPLE NITROGEN COMPOUNDS

This scheme of analysis is subdivided into Section A and Section B. In Section A are included those compounds which contain oxygen-linked nitrogen atoms, and the substances which do not, as a general rule, evolve ammonia or amines on treatment with alkali, and which are usually insoluble in dilute acids. In Section B are grouped those compounds which are substituted ammonia compounds, and therefore usually yield ammonia or amines on treatment with alkalies. Many such compounds are basic in character and are therefore soluble in dilute acids. The results obtained by the preliminary tests will indicate to which section the substance under examination belongs.

TABLE VIII

General Table of Analysis of Nitrogen Compounds

Section A.—Substances which are usually derived from nitric or nitrous acids, and contain oxygen-linked nitrogen atoms. As a rule these substances do not evolve ammonia or amines by the action of strong alkali, nor are they usually soluble in dilute hydrochloric acid, unless they also contain amino-groups.

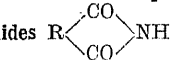
Reduce with Sn and HCl, add NaOH in excess. Diazotise the liberated amine with HNO_2 in the cold and add to β-naphthol dissolved in NaOH solution. The production of a highly coloured dyestuff shows the presence of:	**Aromatic Nitro-Compounds** $Ar.NO_2$	Usually pale yellow in colour. Inflammable. Nitrophenols are soluble in alkalies with intense colours.
	Azoxy-Compounds Ar.N.O.N.Ar	All coloured.
	Azo-Compounds Ar.N : N.Ar	All highly coloured.
	Nitroso-Compounds Ar.NO	Nitroso-phenols, *p*-HO.Ar.NO are usually coloured, soluble in alkalies and reprecipitated by acids. Nitroso-amines, *p*-R_2N.Ar.NO, are usually green in colour, soluble in acids forming yellow hydrochlorides and re-precipitated as green solids by the addition of alkali.

For additional tests, see page 204.

General Table of Analysis of Nitrogen Compounds—*continued.*

Dissolve the merest trace of diphenylamine in a warm mixture of 4 c.c. conc. H_2SO_4 and 1 c.c. of water. Cool and add a very little of the substance.	**Alkyl Nitrates** $R.ONO_2$ **Alkyl Nitrites** $R.ONO$	Rapidly hydrolysed and dissolved by NaOH solution yielding an alcohol and a nitrate or nitrite.
An intense blue colour is developed by all substances that liberate HNO_2 or HNO_3 on treatment with H_2SO_4.	**Nitrosamines** 	Nitrosamines dissolved with an equal quantity of phenol in conc. H_2SO_4 give a blue solution, which with excess of water gives a brownish precipitate, and then an intense blue colour on the addition of an excess of NaOH (*Liebermann's Reaction*). Nitrosamines are not readily attacked by alkalies.
	Aliphatic Nitro Compounds $R.NO_2$	Colourless oils, which yield precipitates with sodium ethylate dissolved in absolute alcohol. These precipitates are violently decomposed by water.
For additional tests, see page 213.		

Section B.—Substances in general that are substituted ammonia derivatives, and which therefore yield ammonia or amines on heating with alkalies or with soda-lime. They are frequently basic in character and insoluble in dilute alkalies.

Add 10 per cent. NaOH solution to the substance, and warm. **Ammonia** readily evolved.	**Ammonium salts** $R.COONH_4$	Usually soluble in water. Identify by examination of the liberated acid, which may or may not contain N.
	Aldehyde Ammonias $R.CHOH.NH_2$	Usually soluble in water. They reduce Tollen's Reagent. Heated with NaOH solution yield coloured or resinous products. Decompose on heating.
	Amides $R.CONH_2$ **Imides** 	Evolve NH_3 on boiling with alkali. The acid obtained on hydrolysis should be identified.
For additional tests, see page 216.	**Nitriles** $R.CN$	React very slowly with boiling alkalies. Often possess an almond-like odour.

General Table of Analysis of Nitrogen Compounds—*continued.*

	Aliphatic Amines, ammoniacal vapour evolved on boiling salts of these amines with NaOH.	See below.
(*a*) Dissolve a little of the substance in dilute HCl, cool thoroughly and add $NaNO_2$ solution drop by drop. (*b*) Add a little of this solution to β-naphthol dissolved in NaOH.	With (*a*) a copious evolution of nitrogen indicates: **Primary Aliphatic Amine**, $R\,NH_2$, whereas with (*b*) the production of an intensely coloured dyestuff indicates **Primary Aromatic Amines**, $ArNH_2$.	On boiling their salts with alkalies, ammoniacal and inflammable gases, with a somewhat fishy odour, are evolved. *For the carbylamine reaction for primary amines, see page* 223. Liberated as oils or solids by heating their salts with alkalies. Usually easily soluble in dilute HCl.
	With (*a*) the separation of a pale yellow oil or solid, which is stable towards alkalies indicates a **Secondary Amine**, R_2NH or Ar_2NH, and the product is a nitrosamine which should be confirmed by the Liebermann Reaction, (page 200).	Secondary amines, like primary amines, may be benzoylated and acetylated. *For Simon's test for secondary amines, see page* 223.
For additional tests for amines and related compounds, see page 223.	With (*a*) the formation of a yellow solution which may yield a yellow precipitate, *and which, on the addition of an excess of alkali precipitates a green base,* indicates an **Aromatic Tertiary amine** of the benzene series, which has a free para-position (*e.g.*, dimethylaniline). The *p*-nitroso - compounds produced do not give the Liebermann reaction (page 200). **Aliphatic Tertiary Amines** do not react at all with HNO_2.	Tertiary amines, either aliphatic or aromatic, cannot be acetylated or benzoylated.

General Table of Analysis of Nitrogen Compounds—*continued.*

If the previous tests have given negative results, attempt to hydrolyse the compounds with boiling conc. HCl (see page 217).	(*a*) Amines are produced by the acid hydrolysis of :	
(*a*) To one part of the solution add an excess of alkali in order to liberate any amine produced by hydrolysis.	**Anilides** Ar.NHCO.R, etc.	Anilides are usually solids, which on boiling with alkalies liberate the base as a solid or liquid. To identify, examine the properties of both the amine and acid produced by hydrolysis.
	Isocyanides R.N : C	Have characteristic and unpleasant odours. On hydrolysis they give primary amines and formic acid.
For additional tests for substances yielding amines on hydrolysis, see page 223.	**Isocyanates** R.N. : CO	Have pungent and irritating odours, react with water and alcohol, and on hydrolysis yield amines and CO_2.
(*b*) To another part of the solution add NaOH until just alkaline and test with Fehling's solution or with ammoniacal silver nitrate.	(*b*) Aldehydes or ketones are produced by the acid hydrolysis of the following compounds, and *the hydrolytic solution also possesses marked reducing properties.*	
For additional tests for those substances yielding aldehydes or ketones on hydrolysis, see page 239.	**Oximes** *e.g.*, $CH_3.CH : NOH$ **Hydrazones** *e.g.*, $CH_3.CH : N.NHC_6H_5$ **Semicarbazones** *e.g.*, $CH_3.CH : N.NH.CO.NH_2$	The liberated aldehyde or ketone should be identified. The powerful reducing properties of the solution are due to the liberated hydroxylamine or hydrazine, etc.

If the substance does not belong to any of the above categories the following special tests should be made for :

Alkaloids

Usually basic and soluble in acids, which solutions give precipitates with iodine in potassium iodide solution (Wagner's Reagent) ; or with mercuric potassium iodide (Mayer's Reagent) ; and with tannic acid (see page 242).

Purines

Respond to the **Murexide Test.** A small quantity of the substance is heated on a crucible lid with one crystal of $KClO_3$, one drop conc. HCl and one drop of water. The whole is evaporated to dryness on a water bath and the residue treated with two to three drops of dilute ammonia, when a pinkish or purple colour is produced (see page 247).

Proteins

Heat a small quantity of the substance in a test tube with about 3 c.c. of **Millon's Reagent** (page 340), when a pink or purple colour is obtained.

In order to definitely establish the nature of the compound under examination, the generic tests for other groups present should be made as directed on page 132, *Table* III. *Finally, to identify the particular substance turn to the detailed tables that follow.*

317. The detailed identification tables that are given in this section are as follows :—

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Solid and Liquid Compounds belonging to the Alkyl Nitrates, Nitrites, the Nitrosamines and Aliphatic Nitro-Compounds	213
Solid Compounds yielding NH_3 on Hydrolysis. Aldehyde-Ammonias, Amides, Imides, Nitriles .	218
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Solid Compounds. Amines and related Compounds yielding Amines on Hydrolysis, such as the Anilides, Hydrazines, iso-Cyanates, iso-Cyanides	226
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Solid Compounds. Hydrazones, Oximes, etc., yielding Aldehydes and Ketones on Hydrolysis .	239
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THE IDENTIFICATION OF AROMATIC NITRO-COMPOUNDS, INCLUDING NITROSO-, AZOXY- AND AZO-COMPOUNDS

318. General Remarks.—Nitro-, nitroso-, azoxy- and azo-compounds, when reduced with tin or zinc in acid solution, yield primary aromatic amines, which may be diazotised and "coupled up" with β-naphthol and thus be identified.

In addition, all these compounds may be reduced by zinc in neutral solution by the Mulliken and Barker reaction. For this reaction dissolve about 0·2 gm. of the substance in 3 c.c. of hot 50 per cent. alcohol, then add a few drops of calcium chloride solution and a little zinc dust. Heat until vigorous boiling takes place, withdraw the flame, and allow the reaction to continue for a few minutes. Filter into a 10 per cent. solution of silver nitrate in concentrated ammonia. A black precipitate of reduced silver, or a silver mirror, will be formed. The reduction of the silver is due to the formation of substituted hydroxylamine derivatives :

$$C_6H_5NO_2 + 4\dot{H} \rightarrow C_6H_5NH(OH) + H_2O.$$

It is, of course, useless to apply this test to compounds which of themselves have the power to reduce ammoniacal silver nitrate.

Nitro-compounds are generally fairly insoluble in water, and have a density greater than water. If they are soluble in alkalies the solution has usually a pronounced colour, as is the case of the nitrophenols. Nitro-compounds are also readily inflammable.

Nitrosophenols are usually coloured; they are soluble in alkalies and are reprecipitated by acids. **Nitroso-tertiary amines** are usually green in colour, and are soluble in acids with the formation of yellow-coloured hydrochlorides (see page 199).

Azo-compounds are highly coloured and stable, so that they can be nitrated and sulphonated. Powerful reducing agents in acid media cause complete rupture of the molecule (see page 97).

$$R.N=N.R + 4\dot{H} \rightarrow RNH_2 + RNH_2.$$

Azoxy-compounds are usually coloured; they can be reduced to azo-compounds by alkaline reducing agents, and to amines by reduction in acid solution. Many azoxy-compounds are converted to azo-compounds by heating with iron filings (see page 113).

319. The Properties of Solid Compounds, containing C.H.[O].N only, of the Aromatic Nitro-, Nitroso-, Azoxy- and Azo-Groups.

M.P. °C.	Colour.	Name.	Characteristics.
36	Yellow	Azoxybenzene $C_6H_5N{-}NC_6H_5$ (O)	Light yellow needles. i.s. water; s. alcohol; v.s. ether, benzene. Reduction in acid solution gives aniline. Heated with iron filings or with PCl_5, gives orange azobenzene, M.P. 68°.
44	Greenish Yellow	*o*-Nitrobenzaldehyde $NO_2.C_6H_4.CHO$	Long needles. Somewhat pungent odour; sternutatory. m.s. hot water; v.s. ether. Forms a sodium bisulphite compound. With cold conc. KOH gives *o*-nitrobenzoic acid, M.P. 144° and *o*-nitrobenzyl alcohol, M.P. 74°. Phenylhydrazone, M.P. 153°.
45	Yellow	*o*-Nitrophenol $HO.C_6H_4.NO_2$	B.P. 214°. Yellow needles of pronounced and characteristic odour. s.s. water; e.s. alcohol, ether. Steam-volatile. Soluble in alkalies with orange colour. Reduced in hot alkaline solution by addition of sodium hydrosulphite; if filtered when hot and the filtrate cooled it gives *o*-amino-phenol, M.P. 165–170°. Acetyl derivative, M.P. 36°, and benzoyl derivative, M.P. 55°, are both colourless, and are formed by the action of the acid chlorides on the sodium salt of the nitrophenol.
54	Colourless	*p*-Nitrotoluene $CH_3.C_6H_4.NO_2$	B.P. 237°. Colourless needles of pronounced aromatic odour. Almost i.s. water; e.s. alcohol and ether. Nitrated with one part fuming HNO_3 and one part conc. H_2SO_4, and gently boiled gives 2:4 dinitro-compound, M.P. 70°. Oxidised by alkaline $KMnO_4$ to *p*-nitrobenzoic acid, M.P. 238°.
54	Colourless	*p*-Nitroanisole $CH_3O.C_6H_4.NO_2$	B.P. 259°. Pronounced aromatic odour. Almost i.s. water; e.s. alcohol, ether. Slightly soluble in NaOH, with yellow colour. Reduced in acid solution gives *p*-anisidine, M.P. 57°. Vigorously nitrated gives symmetrical trinitroanisole (lemon-yellow), M.P. 64°.

The Properties of Solid Compounds—*continued.*

M.P. °C.	Colour.	Name.	Characteristics.
58	Greenish yellow	α-Nitronaphthalene $C_{10}H_7.NO_2$	B.P. 304°. Fine needles. Almost i.s. water; s.s. alcohol; e.s. ether. Reduction in acid media gives α-naphthylamine, M.P. 49°.
68	Orange	Azobenzene $C_6H_5N : NC_6H_5$	B.P. 296°. Almost i.s. water; m.s. alcohol. Reduced by zinc dust in aqueous alcoholic NaOH, or by Zn in glacial acetic acid, to hydrazobenzene, M.P. 126°, which on warming with conc. HCl is converted to benzidine, M.P. 127°. Br in glacial acetic acid gives dibrom-compound, M.P. 187°.
70	Colourless	2 : 4 Dinitrotoluene $CH_3.C_6H_3.(NO_2)_2$	Odourless. Almost i.s. water; s.s. alcohol; e.s. ether. Reduced in acid solution yields corresponding diamine (pale yellow), M.P. 99°.
71	Orange	*o*-Nitroaniline $NO_2.C_6H_4.NH_2$	Odourless. s.s. hot water; e.s. alcohol, ether. Steam-volatile. Primary amine, giving carbylamine reaction and forming diazonium salts. Reduced in acid medium gives *o*-phenylene diamine (extract with ether, after making alkaline), M.P. 102°. With acetic anhydride and one drop H_2SO_4 gives yellow silken needles of *o*-nitro-acetanilide, M.P. 91°.
74	Colourless	*o*-Nitrobenzyl Alcohol $CH_2OH.C_6H_4.NO_2$	Needles. s.s. water; e.s. alcohol, ether. With acid $KMnO_4$ gives *o*-nitro-benzaldehyde, M.P. 44°, and with alkaline $KMnO_4$ gives *o*-nitrobenzoic acid, M.P. 144°. Benzoyl derivative, M.P. 94°.
82	Colourless	sym. Trinitrotoluene $CH_3.C_6H_2.(NO_2)_3$	Odourless. Almost i.s. water; s. alcohol, ether. Soluble in NaOH with formation of red colour. Explosive.

The Properties of Solid Compounds—*continued.*

M.P. °C.	Colour.	Name.	Characteristics.
85	Dark Green	*p*-Nitrosodimethylaniline $NO.C_6H_4.N.(CH_3)_2$	Almost i.s. water; v.s. alcohol, ether. Forms yellow hydrochloride with HCl. Nitrated in the cold with one part pure HNO_3 and one part water, gives dinitrodimethylaniline (yellow), M.P. 86°. Heated with 40 per cent. KOH solution, gives potassium *p*-nitrosophenol and dimethylamine.
90	Yellow	*m*-Dinitrobenzene $C_6H_4(NO_2)_2$	B.P. 297°. s.s. hot water; e.s. alcohol, ether. Reduced in acid solution to *m*-phenylene diamine, M.P. 63°. Quite soluble in water, but can be extracted with ether after addition of alkali. Reduced by boiling with Na_2S and S gives *m*-nitroaniline, M.P. 114°.
92	Pale Yellow	*o*-Nitroacetanilide $NO_2.C_6H_4.NH.COCH_3$	m.s. water; v.s. alcohol, ether. Soluble in aqueous alkalies giving a yellow solution. Saponified on heating with alkalies yielding *o*-nitraniline, orange needles, M.P. 71°.
93	Colourless	*p*-Nitrobenzyl Alcohol $NO_2.C_6H_4.CH_2OH$	Colourless needles; e.s. hot water. Oxidised by acid $KMnO_4$ to *p*-nitrobenzaldehyde, M.P. 106°, and by alkaline $KMnO_4$ to *p*-nitrobenzoic acid, M.P. 238°.
96	Yellow	*m*-Nitrophenol $HO.C_6H_4.NO_2$	Faint odour. Not volatile in steam. Soluble in hot water and alcohol. Soluble in alkalies with orange-red colour. Violet-red colour with $FeCl_3$. Benzoyl derivative, M.P. 95°, and Acetyl derivative, M.P. 55°, are both white in colour, and are obtained by the action of the acid chlorides on the sodium salt of the nitrophenol.
106	Colourless	*p*-Nitrobenzaldehyde $NO_2.C_6H_4.CHO$	Almost colourless. Faint odour. s.s. water, alcohol; m.s. ether. Forms a bisulphite compound, and reduces Tollen's Reagent. Oxidised by alkaline $KMnO_4$ to *p*-Nitrobenzoic acid, M.P. 238°. Phenylhydrazone, red in colour, M.P. 156°.

The Properties of Solid Compounds—*continued.*

M.P. °C.	Colour.	Name.	Characteristics.
109	Brown	α-Nitroso-β-Naphthol $HO.C_{10}H_6.NO$ or $O=C_{10}H_6=NOH$ (Cobalt Reagent)	Tautomeric with β-Naphthoquinone-oxime. e.s. alcohol, ether. Steam-volatile. Na salt green, and precipitated from alcoholic solution with alcoholic NaOH. Oxidised by dilute HNO_3 to α-nitro-β-naphthol, M.P. 103° (yellow crystals). Solution in acetic acid (50 per cent. solution) gives black precipitate of ferric salt with $FeCl_3$; copper and cobalt are also precipitated quantitatively. The Co salt is brick-red in colour. Nickel is not precipitated.
114	Colourless	*p*-Nitrophenol $HO.C_6H_4.NO_2$	Faint odour. e.s. hot water, alcohol, ether. Not volatile in steam. Soluble in alkalies with orange colour. Violet-red colour with $FeCl_3$. Reduced with sodium hydrosulphite (see orthonitrophenol, M.P. 45°) yields *p*-amidophenol, nearly colourless, M.P. 180–185° *d.* Acetyl derivative, M.P. 76°, and benzoyl compound, M.P. 142°, are both colourless and are obtained by the action of the acid chlorides on the sodium salt of the nitrophenol.
114	Golden	*m*-Nitroaniline $NO_2.C_6H_4.NH_2$	B.P. 285°. Steam-volatile. Soluble in hot water, alcohol, ether, and dilute acids. Primary amine. Reduction in acid solution yields *m*-phenylene diamine, M.P. 63°, easily soluble in water, but can be extracted with ether. Treated with acetic anhydride and one drop of conc. H_2SO_4 yields white, compact *m*-nitroacetanilide, M.P. 150–151°.
114	Pale Yellow	2 : 4-Dinitrophenol $HO.C_6H_3.(NO_2)_2$	Odourless. Soluble in hot water. alcohol, ether. Steam-volatile. Soluble in alkalies with yellow colour. Alcoholic $FeCl_3$ gives orange-red colour. Golden-coloured Na salt precipitated in alcoholic solution. Benzoyl derivative, M.P. 213°.

The Properties of Solid Compounds—*continued.*

M.P. °C.	Colour.	Name.	Characteristics.
115	Greenish Blue	*p*-Nitrosomethylaniline $NO.C_6H_4.NH.CH_3$	s.s. water. e.s. alkalies and reprecipitated by CO_2. Soluble in acids. Boiled with 40 per cent. KOH solution yields methylamine and potassium salt of *p*-nitrosophenol.
121	Yellow	2.4.6-Trinitrobenzene $C_6H_3.(NO_2)_3$	Odourless. Almost i.s. water; m.s. alcohol. Soluble in aqueous alkalies with reddish colour. Forms an addition compound, orange in colour, with aniline from alcoholic solution, M.P. 124°.
121	Yellow	Picric Acid 2.4.6-Trinitrophenol $HO.C_6H_2.(NO_2)_3$	Odourless. Very bitter taste. Explosive. Soluble in hot water and in alkalies with increased colour. Dyes the skin or wool bright yellow. Yellow Na salt precipitated in alcoholic solution. Pyridine picrate, yellow needles from aqueous alcohol, M.P. 166°. Dissolve 0·10 gm. naphthalene and 0·20 gm. picric acid in 4 c.c. boiling absolute alcohol and cool. The picrate of naphthalene forms fine yellow needles, M.P. 150°.
120–130 *d.*	Yellowish Green	*p*-Nitrosophenol $O{=}C_6H_4{=}NOH$ or $HO.C_6H_4.NO$	Tautomeric with Benzoquinoneoxime. Faint pungent odour. m.s. water (pale green solution); e.s. alkalies (red solution), alcohol, ether. s.s. benzene. Treated with pure nitric acid gives 2 : 4 dinitrophenol, M.P. 114°. Reduced with sodium hydrosulphite (like *p*-nitrophenol) to *p*-amidophenol, M.P. 180–185° *d.*
125	Orange	*p*-Aminoazobenzene $NH_2.C_6H_4N{=}N.C_6H_5$	B.P. 365°. s.s. hot water; s. alcohol, ether. Primary amine. Dyes wool a yellow colour. The hydrochloride may be crystallised in bluish needles from dilute HCl. Reduced with Sn and HCl gives aniline and *p*-phenylene diamine—make alkaline and steam distil to separate the aniline and then extract the diamine with ether from alkaline residue, M.P. 140°.

The Properties of Solid Compounds—*continued.*

M.P. °C.	Colour.	Name.	Characteristics.
140	Colourless	*m*-Nitrobenzoic Acid $NO_2.C_6H_4.COOH$	Odourless leaflets. m.s. hot water; e.s. ether. Heated with soda-lime gives nitrobenzene. Reduced with Sn and HCl gives *m*-aminobenzoic acid (amphoteric). When the reduction is complete, precipitate the Sn in solution with H_2S, filter and evaporate the filtrate to dryness. Dissolve residue in a little NH_4OH and precipitate amino-acid by just making acid with acetic acid in the cold. The product crystallises in yellowish needles, M.P. 170°. Ethyl *m*-nitrobenzoate, M.P. 47°, B.P. 296°. Chloride, M.P. 30°.
146	Colourless	*o*-Nitrobenzoic Acid $NO_2.C_6H_4.COOH$	Odourless. Solution very sweet to the taste. m.s. hot water; e.s. alcohol, ether. Reduced with Sn and HCl as described under *m*-nitrobenzoic acid (M.P. 140°), gives *o*-aminobenzoic acid, M.P. 144°. Distilled with soda-lime gives nitrobenzene. Ethyl ester, M.P. 30°.
146	Yellow	*p*-Nitraniline $NH_2.C_6H_4.NO_2$	Odourless. s.s. hot water; e.s. alcohol. Not volatile in steam. Primary amine. Reduction with Sn and HCl gives *p*-phenylene diamine, which can be extracted with ether after making alkaline, and has M.P. 140°. Acetylation with acetic anhydride and one drop conc. H_2SO_4 gives colourless *p*-nitroacetanilide, M.P. 210°.
179	Pale Yellow	2.4-Dinitrobenzoic Acid $(NO_2)_2.C_6H_3.COOH$	m.s. hot water, and melts under hot water. v.s.s. benzene. Reduction with Sn. and HCl gives *m*-phenylene diamine *and* CO_2, the diamine may be extracted with ether after making alkaline, M.P. 63°. Ethyl ester, M.P. 41°. Methyl ester, 70°.

The Properties of Solid Compounds—*continued.*

M.P. °C.	Colour.	Name.	Characteristics.
188	Brown	Picramide 2.4.6-Trinitroaniline $NH_2.C_6H_2.(NO_2)_3$	i.s. water; s. alcohol. Boiled with conc. alkalies yields ammonia and picric acid, forming an orange solution. Reduction products unstable.
210	Colourless	*p*-Nitroacetanilide $NO_2.C_6H_4.NH.COCH_3$	m.s. hot water, e.s. alcohol, conc. H_2SO_4 (colourless) and in cold NaOH (orange solution). The solution in alkalies is readily decomposed on heating, and *p*-nitraniline, yellow, M.P. 146°, separates on cooling. Vigorous reduction in acid solution gives *p*-phenylene diamine, which is extracted with ether after making alkaline, M.P. 140°.
235	Yellow	*p*-Nitrobenzoic Acid $NO_2.C_6H_4.COOH$	Soluble in hot water, alcohol; v.s. ether. Heated with soda-lime gives nitrobenzene. Reduction with Sn in acid solution gives *p*-aminobenzoic acid, M.P. 185°, which is separated as described under *m*-nitrobenzoic acid (M.P. 140°). Methyl ester, M.P. 96°. Ethyl ester, M.P. 57°. Chloride, M.P. 75°.
240	Colourless	*o*-Nitrocinnamic Acid $NO_2.C_6H_4.CH:CH.COOH$	Faint odour. i.s. water; m.s. alcohol. Warmed with conc. H_2SO_4 gives blue colour. Unsaturated. Boiled with alkaline $KMnO_4$ yields *o*-nitrobenzoic acid (M.P. 146°). Ethyl ester, M.P. 42°. Methyl ester, M.P. 72°. Chloride, M.P. 64°.
284	Pale Yellow	*p*-Nitrocinnamic Acid $NO_2C_6H_4.CH:CH.COOH$	s.s. hot water, ether; m.s. alcohol. Soluble in warm H_2SO_4 with yellow colour. Unsaturated. Boiled with alkaline $KMnO_4$ yields *p* nitrobenzoic acid (M.P. 235°). Ethyl ester, M.P. 138°. Methyl ester, M.P. 161°.

320. Properties of Liquid Compounds, containing C.H.[O].N only, of the Aromatic Nitro-, Nitroso-, Azoxy- and Azo-Groups.

B.P. °C.	Δ	Name.	Characteristics.
209	1·212 (13°)	Nitrobenzene $C_6H_5.NO_2$	M.P. 5°. Odour of almonds. Yellow colour. Steam-volatile. Almost i.s. water; v.s. alcohol, ether. Reduction in acid solution yields aniline—make alkaline, steam distil, and test distillate, after addition of water, with bleaching powder, gives violet coloration. Nitration with fuming HNO_3 gives *m*-dinitrobenzene (M.P. 90°).
220	1·168 (15°)	*o*-Nitrotoluene $CH_3.C_6H_4.NO_2$	M.P. −10°. Odour of almonds. Yellow colour. Steam-volatile. Almost i.s. water; miscible with alcohol, ether. Nitrated with equal parts conc. H_2SO_4, and fuming HNO_3 at 100°, yields yellow 2 : 4 dinitrotoluene (M.P. 70°). Oxidised with alkaline $KMnO_4$ yields *o*-nitrobenzoic acid (M.P. 146°). Reduction in acid solution gives *o*-toluidine, B.P. 199°, which gives brown colour with bleaching powder, and forms an acetyl derivative, M.P. 110°.
232	1·168 (22°)	*m*-Nitrotoluene $CH_3.C_6H_4.NO_2$	M.P. 15°. Faint almond odour. Yellow colour. Almost i.s. water; miscible with alcohol, ether. Reduction in acid solution yields *m*-toluidine, B.P. 203°, which on acetylation gives acet-*m*-toluidide, M.P. 65°.
265	1·268 (20°)	*o*-Nitroanisole $NO_2.C_6H_4.OCH_3$	Aromatic odour. M.P. 9° C. Yellow. Almost i.s. water; e.s. alcohol, ether. Reduction in acid solution gives *o*-anisidine, B.P. 234°.

THE IDENTIFICATION OF ALKYL NITRATES AND NITRITES, NITROSAMINES AND THE ALIPHATIC NITRO-COMPOUNDS

321. General Remarks.—As indicated in the systematic table of analysis for nitrogen-containing substances (page 200), all these classes of compounds liberate nitrous or nitric acid by the action of strong sulphuric acid, and, therefore, give the diphenylamine test. As this test is particularly delicate, care must be taken that other substances, such as aromatic nitro-compounds that have been prepared by the agency of nitric acid or nitrous acid, are uncontaminated by excess of these reagents, or else they will also give positive results in this test.

Alkyl nitrates and nitrites may be further distinguished by the fact that they are rapidly hydrolysed and dissolved by alkalies on warming, producing alcohols and salts of nitrous or nitric acid. The nitrous acid so obtained may be identified by the fact that the diazotisation of aniline may be carried out by its agency.

The Nitrosamines are not readily attacked by alkalies and answer to Liebermann's reaction (see page 200). They are either yellow oils or solids of fairly low M.P.

The Aliphatic Nitro-compounds are colourless oils, and yield precipitates in absolute alcoholic solution with sodium ethylate. These precipitates are explosive, and are *usually decomposed with violence by the action of water.*

Since these types of compounds all respond to the same generic test they are classified together in the detailed tables that follow.

322. The Properties of Solid Compounds, containing C.H.[O].N only, belonging to the Alkyl Nitrates, Nitrites, the Nitrosamines and the Aliphatic Nitro-compounds.

M.P. °C.	Colour.	Name.	Characteristics.
58	Yellow	Benzyl Phenyl Nitrosamine C_6H_5 $C_6H_5.CH_2$ >N.NO	Is the nitrosamine of benzylaniline. Needles. e.s. alcohol, ether. Yields benzalaniline, M.P. 54°, on warming with alcoholic HCl.

The Properties of Solid Compounds—*continued.*

M.P. °C.	Colour.	Name.	Characteristics.
66	Yellow	Diphenyl Nitrosamine $(C_6H_5)_2 : N.NO$	The nitrosamine of diphenylamine. e.s. hot alcohol, ether. Soluble in conc. H_2SO_4 with intense blue colour. Warmed with alcoholic HCl yields *p*-nitrosodiphenylamine of M.P. 144°, which is liberated from the solution as a green solid on the addition of alkali.

323. The Properties of Liquid Compounds, containing C.H.[O].N only, belonging to the Alkyl Nitrates, Nitrites, the Nitrosamines and the Aliphatic Nitro-compounds.

B.P. °C.	Δ	Name.	Characteristics.
17	0·900 (15°)	Ethyl Nitrite $C_2H_5.ONO$	Pleasant odour. s.s. water; miscible with alcohol. Easily saponified.
66	1 232 (5°)	Methyl Nitrate $CH_3.ONO_2$	Pleasant odour. Almost i.s. water. Explodes on sudden heating. Easily saponified.
87	1·115 (15°)	Ethyl Nitrate $C_2H_5.ONO_2$	Pleasant odour. Almost i.s. water. Easily saponified.
95	0·880 (15°)	Isoamyl Nitrite $C_5H_{11}.ONO$	Yellow oil of characteristic and penetrating odour. s.s. water. Easily saponified.
101	1·145 (15°)	Nitromethane $CH_3.NO_2$	Colourless. Pleasant odour. s. water. Yields a precipitate with sodium ethylate. Reduced with NaOH and Zn dust, on warming evolves methylamine. Heated in a sealed tube with excess HCl yields hydroxylamine hydrochloride, which can be detected by its reducing properties $CH_3NO_2 + H_2O + HCl \longrightarrow H.COOH + NH_2OH.HCl$
114	1 101 (0°)	Nitroethane $C_2H_5.NO_2$	Colourless. Sweetish odour. s. water. Yields a white precipitate with sodium ethylate. Reduction with Zn in NaOH on boiling evolves ethylamine. Yields hydroxylamine with HCl similarly to nitromethane.

The Properties of Liquid Compounds—*continued.*

B.P. °C.	Δ	Name.	Characteristics.
152	—	Dimethyl Nitrosamine $(CH_3)_2 : N.NO$	Yellow oil of characteristic odour. i.s. water; s. alcohol. Boiled with alcoholic HCl yields dimethylamine, which is liberated on the addition of alkali.
175	0·960 (15°)	Diethyl Nitrosamine $(C_2H_5)_2 : N.NO$	Yellow oil with odour of mint. i.s. water; s. alcohol. Boiled with alcoholic HCl yields diethylamine, which is liberated on the addition of alkali.
225*d.*	—	Methyl Phenyl Nitrosamine 	Yellow oil, aromatic odour. i.s. water; e.s. alcohol. Boils with decomposition but may be steam-distilled unchanged. Warmed with alcoholic HCl yields *p*-nitroso-methylaniline hydrochloride, from which the base may be liberated, in the form of blue needles, by the addition of alkali, M.P. 114°.

THE IDENTIFICATION OF COMPOUNDS EVOLVING AMMONIA ON HYDROLYSIS WITH ALKALIES

324. General Remarks.—Ammonia is evolved by the alkaline hydrolysis of ammonium salts, aldehyde-ammonias, amides, imides and nitriles. The procedure to be adopted with these compounds is outlined in the following table :—

TABLE IX

A. Ammonia evolved readily on gently warming with NaOH.

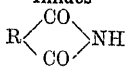
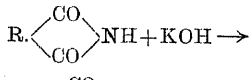
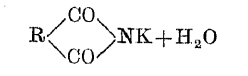
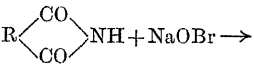
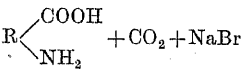
Aldehyde-ammonias $R.CH.OH.NH_2$	Usually soluble in water and decomposed on heating alone, with effervescence. They reduce Tollen's reagent. On hydrolysis with NaOH the solution turns yellow on further heating, and resinous compounds are often formed.	To identify, distil with dilute sulphuric acid and examine the liberated, volatile aldehyde (see also paragraph 326).
Ammonium Salts $R.COONH_4$	Usually soluble in water. Evolve ammonia slowly on heating with magnesium oxide and water, and may be distinguished in this way from amides, imides, and nitriles.	To identify, add an excess of HCl and separate the liberated acid by filtration, distillation or extraction with ether. Determine the elements present in the acid, and then identify in the usual manner.

B. Ammonia evolved on boiling with NaOH.

Amides $R.CONH_2$	Amides and imides should be hydrolysed as directed in paragraph **325** below, and the resultant acid separated by filtration, distillation or extraction with ether, and identified in the usual manner. The nature of the compounds may be confirmed by the tests given in the adjacent column, and by the particular tests tabulated in paragraph **326**.	**Amides** on treatment with P_2O_5 yield nitriles, which may be extracted with ether after the addition of water. $R.CONH_2 \longrightarrow R.C:N+H_2O$ Amides on treatment with Br and excess of NaOH solution yield amines, which may be distilled and absorbed in HCl and then identified. $R.CONH_2+NaOBr \longrightarrow R.NH_2+CO_2+NaBr$ (see Preparation 66, page 99).

Table IX.—*continued.*

B. Ammonia evolved on boiling with NaOH—*continued.*

Imides 		**Imides** on treatment with cold alcoholic KOH usually give a precipitate of the potassium salt.   With Br and excess of NaOH solution they give an amino-acid, and not a simple amine.  

C. Ammonia evolved only very slowly on boiling with alkali.

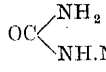
Nitriles R.C : N	Nitriles often possess an odour of almonds. To identify nitriles, they should be hydrolysed as directed in paragraph **325** below. Particular tests for individual nitriles are tabulated in paragraphs **326** and **327**.	On reduction with Sn and HCl, nitriles yield primary amines, which are liberated on the subsequent addition of alkali. $R.CN + 4H \longrightarrow R.CH_2.NH_2$ Nitriles are converted to amides by the action of H_2O_2 and warm NaOH solution (see Preparation 54, page 83).

325. The Hydrolysis of Amides, Nitriles and similar Compounds by the Action of Acid.

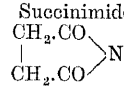
It is usually advantageous to saponify amides and related compounds by the action of hydrochloric acid, as both sulphuric acid and strong alkali are liable to give very discoloured reaction products. The hydrolysis is effected by refluxing together for twenty minutes, or longer, about 2 gm. of the substance with 20 c.c. of pure HCl and 10 c.c. of water. The acid produced, if solid, should be separated by filtration. If liquid it may be separated by distillation or by extraction with ether. Its properties should then be examined.

If the original substance is very insoluble in hydrochloric acid, the saponification should be effected with 50 per cent. sulphuric acid, or with 15–20 per cent. alcoholic potash.

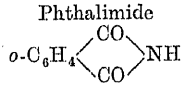
326. Properties of Solid Compounds, containing C.H.[O].N only, that yield Ammonia on Hydrolysis, e.g., Aldehyde-Ammonias, Amides, Imides, Nitriles.

M.P. °C.	B.P. °C.	Name.	Characteristics.
38	217	*p*-Tolunitrile $CH_3.C_6H_4.CN$	Usually melts about 29–30° C. Colourless, crystalline mass with odour of almonds. Almost i.s. water; e.s. alcohol. Best saponified with alcoholic KOH, yielding *p*-toluic acid, M.P. 176°.
49	180	Urethane, Ethyl Carbamate $NH_2.COOC_2H_5$	Colourless needles. v.s. water, alcohol, ether. On hydrolysis yields NH_3, C_2H_5OH and CO_2. Warmed with NaOH and iodine gives faint iodoform reaction.
52	177	Methyl Carbamate $NH_2.COOCH_3$	Colourless needles. v.s. cold water; e.s. alcohol. Hydrolysis gives NH_3, CH_3OH and CO_2.
79	213	Propionamide $C_2H_5.CONH_2$	Colourless leaflets. s. water, alcohol. Hydrolysis gives propionic acid and NH_3.
82	222	Acetamide $CH_3.CONH_2$	Usually has lower M.P. than given, and a pronounced mouse-like odour. Colourless needles. v.s. cold water, alcohol; s.s. ether. Hydrolysis gives acetic acid and NH_3.
95	*d.* 100	Acetaldehyde Ammonia $CH_3.CH.(OH).NH_2$	Colourless crystals that soon become yellow. Faint, sharp odour. e.s. water, alcohol; s.s. ether. Strongly alkaline. Warmed with dilute acids yields acetaldehyde. Warmed with NaOH yields NH_3 and solution becomes yellow and turbid due to the formation of aldehyde resin. Reduces Tollen's Reagent.
96	*d.*	Semicarbazide 	Colourless crystals that decompose on keeping. e.s. water, alcohol. Powerful reducing agent, reducing both Fehling's solution and Tollen's reagent in the cold. Hydrochloride, M.P. 175° *d.* Benzaldehyde semicarbazone, M.P. 213°.

Properties of Solid Compounds—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
124	287	Succinimide 	Small odourless crystals. v.s. water, alcohol; s.s. ether. Hydrolysis gives succinic acid and NH_3. Heated with excess Zn dust yields pyrrole, which can be detected by introducing a pine splinter soaked in conc. HCl into the tube.
126	291 *d.*	Benzamide $C_6H_5.CONH_2$	Odourless crystals, distilling with decomposition and odour of almonds ($C_6H_5.CN$), s.s. water; e.s. alcohol, ether. Hydrolysis gives benzoic acid and NH_3.
132	*d.*	Urea Carbamide $CO(NH_2)_2$	Colourless, odourless prisms or needles with salt taste. v.s. water; m.s. alcohol. Heat in a tube over a small flame for one minute, cool, and dissolve the residue in a small quantity of water and add a little dilute NaOH and then $CuSO_4$ solution drop by drop. A reddish violet colour is obtained (**Biuret Reaction**). Conc. HNO_3 added to a strong aqueous solution precipitates urea nitrate in small crystals. NaOBr solution yields nitrogen gas. Hydrolysis yields NH_3 and CO_2.
138	270 *d.*	Salicylamide $o\text{-}C_6H_4.(OH).CONH_2$	White crystals. s.s. water; e.s. alcohol, ether. Faintly acid in reaction. Soluble in Na_2CO_3 solution without decomposition. Hydrolysed, preferably with alcoholic KOH, yielding salicylic acid and ammonia.
147	*d.*	Phenylurea (Phenylcarbamide) $C_6H_5.NH.CO.NH_2$	Odourless crystals. e.s. hot water, alcohol, ether. Saponified easily, yielding NH_3, CO_2 and aniline. Gives the carbylamine reaction for primary amines. Boiled with aniline yields carbanilide, M.P. 236°, the excess of aniline is removed with dilute HCl, and the product recrystallised from aqueous alcohol.

Properties of Solid Compounds—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
154	280	Phenylacetamide $C_6H_5.CH_2.CONH_2$	Colourless crystals. e.s. hot water, alcohol. Often boils with decomposition somewhat below temperature stated. Hydrolysed with HCl, yields NH_3 and phenylacetic acid. Boiled with water and HgO yields a white crystalline double compound, M.P. 206°.
170	*d.*	Malonamide $CH_2.(CONH_2)_2$	Colourless. e.s. water; v.s.s. alcohol. Hydrolysed with HCl yields NH_3 and malonic acid.
188 *d.*	*d.*	Biuret $NH.(CONH_2)_2+H_2O$	Colourless, odourless crystals. e.s. hot water, alcohol; s.s. ether. Strongly heated yields NH_3. Heated with NaOH solution yields NH_3. Gives Biuret Reaction, see Urea (M.P. 132°).
Sublimes 225–230 with decomp.	*d.*	Asparagine $CH_2.CONH_2$ | $CH.NH_2.COOH$	Colourless crystals. Acid in reaction e.s. hot water; v.s.s. cold alcohol, ether. Lævo-rotatory in water, dextro-rotatory in HCl. Saponification yields NH_3 and aspartic acid, M.P. 270° *d.*
229	—	Phthalimide 	Flat, odourless needles. i.s. water; s. alcohol, strong KOH. Yields precipitate of K salt with alcoholic KOH. Saponified yields ammonia and phthalic acid. Gently heated with resorcin and conc. H_2SO_4 yields orange solution, which on pouring into NaOH solution gives the fluoresceïn reaction (see page 125).
280 in sealed tube.	—	Hexamethylene-tetramine Hexamine Urotropine $C_6H_{12}N_4$	Condensation product of NH_3 and formaldehyde. Colourless, odourless crystals. Alkaline in reaction. v.s. water; s.s. alcohol; i.s. dry ether. Heated with dilute acids yields formaldehyde and NH_3. Yields a white crystalline compound with a strong solution of $HgCl_2$, which after recrystallisation from water has M.P. 220–230° *d.*

Properties of Solid Compounds—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
415 in sealed tube.	—	Oxamide $\begin{matrix}CONH_2\\ \vert\\ CONH_2\end{matrix}$	Odourless powder. i.s. water, alcohol, ether. Heated in open tube sublimes with some decomposition, yielding C_2N_2. Hydrolysed with alkalies yields NH_3 and oxalic acid.
—	—	Guanidine Carbonate $HN : C(NH_2)_2.H_2CO_3$	Guanidine itself is a deliquescent mass, strongly alkaline, and usually only obtained in the form of its salts. It is unstable and easily oxidised. Guanidine carbonate does not melt below 360°; evolves CO_2 with acids. v.s. water. With HNO_3 yields a sparingly soluble nitrate, M.P. 215°, and with saturated picric acid solution yields a picrate, M.P. 320°. Guanidine and its salts are hydrolysed with alkalies, and yield NH_3 and CO_2.

327. Properties of Liquid Compounds, containing C.H.[O].N only, which yield Ammonia on Hydrolysis—Amides, Imides, Nitriles.

B.P. °C.	Δ	Name.	Characteristics.
81	0·791 (14°)	Acetonitrile $CH_3.CN$	Pleasant odour. Miscible with water. Burns with a peach-coloured flame. Saponified with alcoholic KOH to NH_3 and acetic acid. With warm NaOH and H_2O_2 yields acetamide.
97	0·787 (15°)	Propionitrile $C_2H_5.CN$	Pleasant odour. e.s. water, but can be salted out. Saponified with alcoholic KOH yields NH_3 and propionic acid.
191	1·000 (25°)	Benzonitrile $C_6H_5.CN$	Strong odour of almonds. Almost i.s. water; miscible with alcohol, ether. Saponified with alcoholic potash yields benzoic acid and NH_3. With NaOH and H_2O_2 (warm) yields benzamide. Reduced with Sn and HCl yields benzylamine, B.P. 182°, which has a strong odour of ammonia.

Properties of Liquid Compounds—*continued.*

B.P. °C.	Δ	Name.	Characteristics.
193 *d.*	1·335 (15°)	Formamide $H.CONH_2$	Odourless liquid. Can only be distilled under reduced pressure. s. water. Easily saponified to NH_3 and formic acid.
205	0·998 (15°)	*o*-Tolunitrile $CH_3.C_6H_4.CN$	Odour of almonds. Colourless liquid. Almost i.s. water; miscible with alcohol, ether. Only saponified with difficulty, yielding *o*-toluamide, M.P. 139°. Complete saponification is very difficult owing to steric hindrance.
233	1·021 (15°)	Phenylacetonitrile Benzyl Cyanide $C_6H_5.CH_2.CN$	Colourless liquid. Almost i.s. water; soluble in alcohol, ether. Saponified with 50 per cent. H_2SO_4 yields NH_3 and phenylacetic acid.

THE IDENTIFICATION OF AMINES AND COMPOUNDS WHICH ON HYDROLYSIS YIELD AMINES

328. General Remarks.—In this section the amines, and such compounds as the anilides, the iso-cyanates, and the iso-cyanides, which yield amines on hydrolysis, are described. Such compounds as the nitro-amines, and a few compounds such as phenylurea that yield ammonia as well as an amine on hydrolysis, have already been considered in the previous sections to which they belong.

The use of **nitrous acid** to distinguish and identify amines has already been given as a generic test in the scheme of analysis, paragraph **316**, page 201. The majority of simple amines are soluble in acids.

Primary amines may also be distinguished by the **carbylamine reaction**; only a very few aromatic compounds of high molecular weight fail to respond to this test. It must be remembered, however, that the test is so delicate that secondary or tertiary amines contaminated with but a very little of the primary amine give positive results. To carry out the reaction dissolve a *small* piece of caustic potash in 2 c.c. of alcohol, add a *small* quantity of the amine and a few drops of chloroform and boil gently, when a strong odour of carbylamine is obtained. If the result is negative, cool and repeat after a few minutes.

$$R . NH_2 + CHCl_3 + 3KOH \rightarrow R . N : C + 3KCl + 3H_2O$$

The majority of the anilides give this reaction, since some of the primary base is liberated by the alcoholic potash. *The nauseating odour should be immediately destroyed by the addition of strong hydrochloric acid, and on no account should the reactants be thrown into the sink before this is done.*

Secondary amines may be distinguished not only by the production of nitrosamines by interaction with nitrous acid, but also, if at all soluble, by **Simon's Reaction.** Prepare a fresh solution of acetaldehyde from a few cubic centimetres of 50 per cent. alcohol by plunging into it a red-hot copper-wire spiral, oxidised superficially in the Bunsen flame. Withdraw the spiral immediately; cool the solution, and repeat the process twice. To one drop of the secondary amine add 2–3 c.c. of water, a trace of dilute sodium nitroprusside solution and 1 c.c. of the freshly prepared aldehyde

solution. A blue coloration, which gradually fades, is slowly developed.

Tertiary amines do not react with nitrous acid, except with compounds of the benzene series, in which the para-position to the amino-group is unoccupied. In this case para-nitroso compounds are formed, which are green solids forming yellow hydrochlorides.

$$C_6H_5 . N(CH_3)_2 + HNO_2 \rightarrow p\text{-}ON . C_6H_4 . N(CH_3)_2 + H_2O$$

Tertiary amines also form addition compounds with methyl iodide, sometimes immediately on mixing, as in the case of quinoline, but often only on refluxing together for some time. It must be remembered that many primary and secondary amines also react with the alkyl iodides.

Primary and secondary amines may be converted into their acetyl, benzoyl or benzene sulphonyl derivatives in order to complete identification. The preparation of these compounds is described in paragraphs **329** and **330** following. Tertiary amines do not, of course, form such compounds.

The Amino-acids are usually much more soluble in water than the simple amines. They are amphoteric in nature.

The Amino-phenols are also amphoteric in nature, they are soluble in alkalies and acids, are moderately soluble in water, and are usually readily oxidised on exposure to the air, particularly in alkaline media, their solutions becoming brown.

The anilides, which are usually solids, are derivatives of primary and secondary amines. They are hydrolysed with acids or alkalies yielding the amines. In order definitely to identify them they should be hydrolysed as described in paragraph **325**, page 217, and the resultant hydrolytic products examined.

The Hydrazines are monacid bases, $R.NH.NH_2$, somewhat easily oxidised in the free state, but more stable in the form of their salts, which are usually fairly soluble in water. From these solutions the hydrazines are precipitated by the addition of alkali as brownish oils or solids. The hydrazines are characterised by their powerful reducing properties, reacting readily with Fehling's solution and with ammoniacal silver nitrate. They react with nitrous acid with the formation of the nitroso-hydrazines.

The iso-Cyanides possess very unpleasant odours. On warming with acids they are hydrolysed, yielding formic acid and primary amines.

$$R.N : C + 2H_2O + HCl \rightarrow H.COOH + R.NH_2.HCl$$

Boiled with mercuric oxide the corresponding iso-cyanates are produced.

$$R.N : C + HgO \rightarrow R.N : CO + Hg$$

The iso-Cyanates possess irritating odours. They are hydrolysed by acid or alkali with the formation of primary amines :

$$2R.N : CO + 2H_2O + 2HCl \rightarrow 2RNH_2.HCl + CO_2$$

The iso-cyanates react with water, alcohols and primary and secondary amines.

329. Acetylation of Amines.—Amines, primary and secondary, form acetyl derivatives which are of value in identification. In order to form the acetyl compound, the amine is either heated with a small excess of acetyl chloride and the product recrystallised from water or aqueous alcohol, or else warmed with acetic anhydride, to which one drop of concentrated sulphuric acid may be added to start the reaction. The product must be recrystallised after boiling with a little alcohol to destroy the excess of reagent. Compare preparation 56, page 84.

330. Benzoylation of Amines.—The usual method used for the benzoylation of amines is the **Schotten-Baumann Reaction,** previously described on page 84. The amine is treated with benzoyl chloride and an excess of aqueous caustic soda solution. The reaction mixture is warmed to destroy the excess of benzoyl chloride and the product recrystallised from aqueous alcohol. In a few cases in the aliphatic series a water-soluble product is obtained which must be extracted with ether.

The amino-acids do not give good yields by the Schotten-Baumann reaction, and should be benzoylated by the **Fischer Benzoylation Reaction,** in which the amino-acid is dissolved in water and treated with considerable excess of sodium bicarbonate and of benzoyl chloride, the latter being added in small instalments and shaken after each addition.

The identification of primary and secondary amines may also be made by the preparation of the **benzene-sulphonyl derivatives (Hinsberg's Reaction).** The amine is treated with benzene sulphonyl chloride as in the Schotten-Baumann reaction. Primary amines form sodium benzene sulphonamides, *soluble* in the alkaline solution, but which can be extracted with ether or precipitated with mineral acid :

$$R \cdot NH_2 + C_6H_5SO_2Cl + 2NaOH \rightarrow NaCl + 2H_2O + \underset{\text{soluble}}{R \cdot N \cdot Na \cdot SO_2 \cdot C_6H_5}$$

$$\xrightarrow[HCl]{} R \cdot NH \cdot SO_2 \cdot C_6H_5 + NaCl$$

Secondary amines form *insoluble* sulphonamides :

$$NaOH + R_2NH + C_6H_5 \cdot SO_2Cl \rightarrow NaCl + H_2O + R_2N \cdot SO_2 \cdot C_6H_5$$

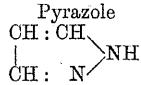
By Hinsberg's reaction, therefore, not only may the primary and secondary amines be identified, but the separation of a mixture of amines may be made.

331. Properties of Solid Substances, containing C.H.[O].N only. The Amines and related Compounds which on Hydrolysis yield Amines.

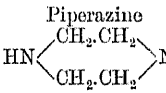
For nitro-amines, see nitro-compounds, page 205. For the alkaloids and purines, see pages 242, 247.

M.P. °C.	B.P. °C.	Name.	Characteristics.
24	135/15 mm.	Methyl Anthranilate Methyl *o*-Aminobenzoate $NH_2.C_6H_4.COOCH_3$	Synthetic perfume. Primary amine. Soluble in water; e.s. alcohol, ether. Solution in alcohol shows a bluish fluorescence. Hydrolysis with alkalies yields anthranilic acid (M.P. 144°) and CH_3OH. Picrate is sparingly soluble in water; forms needles. M.P. 105°.
32	298	Benzylaniline	See page 238. Usually liquid.
43	200	*p*-Toluidine $CH_3.C_6H_4.NH_2$	Faint, peculiar odour. Primary amine. Solution in two parts of H_2SO_4, and one part of water gives a coloured ring on the addition of 2–3 drops HNO_3 without shaking; the colour gradually changes from blue to red. Acetyl derivative, M.P. 146°. Benzoyl derivative, M.P. 155°. No colour with bleaching powder.
46	284	Formanilide $C_6H_4.NH.OCH$	White plates. e.s. hot water, alcohol. Readily gives carbylamine reaction. Hydrolysis with HCl yields aniline and formic acid. Yields a precipitate of the Na salt in alcoholic solution.
49	301	*α*-Naphthylamine $C_{10}H_7.NH_2$	Unpleasant, persistent odour. Primary amine. Discolours on keeping. s.s. hot water; e.s. alcohol, ether. Solution in HCl gives bluish precipitate on heating with a little $FeCl_3$ solution. Acetyl derivative, M.P. 159°. Benzoyl derivative, M.P. 156°. Picrate, M.P. 160–165° *d*.

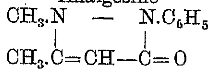
Properties of Solid Substances—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
54	302	Diphenylamine $(C_6H_5)_2.NH$	Lustrous plates. Faint odour. i.s. water; e.s. alcohol, ether. Feebly basic and almost insoluble in dilute acids. Solution in 66 per cent. H_2SO_4 gives intense blue colour with trace of HNO_3. Secondary amine yielding from solution in alcohol a nitrosamine of yellow colour, with M.P. 66°. Acetyl derivative, M.P. 101°. Benzoyl derivative, M.P. 177°.
57	245	*p*-Anisidine $NH_2.C_6H_4.OCH_3$	White needles of faint odour. s. hot water; e.s. alcohol, ether. Primary amine. Solution in HCl warmed with $FeCl_3$ yields violet-red colour. Acetyl derivative, M.P. 125°. Benzoyl derivative, M.P. 153°.
63	283	*m*-Phenylenediamine $C_6H_4.(NH_2)_2$	Colourless needles, rapidly darkening on exposure. e.s. water with alkaline reaction; e.s. alcohol, ether. Solution in acid yields coloured precipitate with $NaNO_2$. Diacetyl derivative (M.P. 191°), dissolved in water and treated with Br water in excess yields a dibromdiacetyl derivative, M.P. 256°. Dibenzoyl derivative, M.P. 240°.
65	303	*m*-Acet-toluidide $CH_3.C_6H_4.NHCOCH_3$	White crystals. Sparingly soluble in water. Hydrolysed with HCl yields *m*-toluidine and acetic acid.
69	187	Pyrazole 	Colourless needles with faint odour. e.s. water, alcohol, ether. $HgCl_2$ yields white precipitate. Ammoniacal $AgNO_3$ gives white precipitate of Ag salt. Picrate, from ether, M.P. 159°.

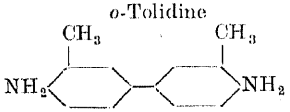
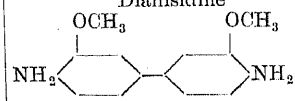
Properties of Solid Substances—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
89	—	Ethyl *p*-aminobenzoate $NH_2.C_6H_4.COOC_2H_5$	"Anæsthesine." Colourless crystals, giving carbylamine reaction only with difficulty. Hydrolysis gives *p*-aminobenzoic acid (amphoteric) and ethyl alcohol. Picrate precipitated in strong solution of hydrochloride has M.P. 129°. Benzoyl derivative, M.P. 148°.
101	257	*o*-Phenylenediamine $C_6H_4(NH_2)_2$	Colourless plates. Odourless. Primary amine. e.s. hot water, alcohol, chloroform. Solution in HCl yields reddish precipitate with $FeCl_3$. Diacetyl derivative M.P. 182°. Dibenzoyl derivative, M.P. 300°.
104	—	Propionanilide $C_6H_5.NH.COC_2H_5$	Colourless plates. s.s. water; e.s. alcohol, ether. Hydrolysed with HCl yields aniline and propionic acid.
105	145	Piperazine 	Deliquescent, odourless crystals, e.s. water, alcohol. Secondary amine, gives Simon's Reaction (page 223). Dinitroso-derivative, white plates, M.P. 157°.
110	296	*o*-Acet-toluidide $CH_3.C_6H_4.NH.COCH_3$	White needles. s.s. water; e.s. alcohol. Gives carbylamine reaction. Hydrolysed with HCl, yields acetic acid and *o*-toluidine.
110	304	*β*-Naphthylamine $C_{10}H_7.NH_2$	White scales. *Odourless.* Primary amine. e.s. hot water, alcohol. Does not give any colour with $FeCl_3$. Acetyl derivative, M.P. 132°. Benzoyl derivative, M.P. 162°.

Properties of Solid Substances—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
112	—	Methyl-*p*-aminobenzoate $NH_2.C_6H_4.COOCH_3$	Colourless plates. Primary amine, but gives carbylamine reaction only with difficulty. s.s. water; e.s. alcohol. Hydrolysed gives *p*-aminobenzoic acid (amphoteric) and CH_3OH.
112	320°/175 mm.	Antipyrine Analgesine 	Colourless plates. Faint odour. Unsaturated. Basic. v.s. water, alcohol; s.s. ether. Nitroso-derivative, green crystals, M.P. 190–195° *d.* Dibromide, from $CHCl_3$ solution has M.P. 148°, and this gives with water brom-antipyrine, M.P. 117°.
114	304	Acetanilide $C_6H_5.NH.COCH_3$	Colourless, odourless crystals. e.s. hot water, alcohol, ether. Gives carbylamine reaction. Hydrolysed with HCl yields aniline and acetic acid. Aqueous solution yields, with Br-water, *p*-brom-acetanilide, M.P. 170°. With HNO_2 in glacial acetic acid gives nitroso-derivative, M.P. 50°.
123	—	*m*-Aminophenol $HO.C_6H_4.NH_2$	White needles, easily oxidised. s. hot water, alcohol, ether, acids and caustic alkalies. Hydrochloride, M.P. 229°. Dibenzoyl derivative, 153°.
126	—	Hydrazobenzene $C_6H_5.NH.NH.C_6H_5$	Lustrous plates, rapidly oxidised, especially in alkaline media. v.s.s. water; e.s. alcohol, ether. Reduces Tollen's reagent. Boiled with HCl gives benzidine, M.P. 127°. Boiled with dilute H_2SO_4 precipitates shimmering crystals of benzidine sulphate. Boiled with alcohol, and a little aqueous $FeCl_3$, yields azo-benzene in orange crystals, M.P. 68°.

Properties of Solid Substances—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
127	405	Benzidine *p.p.*-$NH_2.C_6H_4.C_6H_4.NH_2$	Lustrous plates, becoming discoloured in air. s.s. hot water; s. alcohol. Primary amine. The sulphate is almost insoluble in water and alcohol, and is thus readily precipitated. The saturated aqueous solution on the gradual addition of **very dilute** Br-water, gives an intense green colour, which with more of the reagent changes to yellow. Diacetyl derivative, M.P. 317°. Boiled in alcoholic solution with benzaldehyde, dibenzylidene-benzidine is obtained in yellowish needles, with M.P. 232°, after recrystallisation.
127	—	Triphenylamine $(C_6H_5)_3N$	Colourless crystals. i.s. water; s.s. alcohol; e.s. ether. Practically neutral in character, not forming salts with any acid. Solution in glacial acetic acid turns green on the addition of a trace of HNO_3, and turns violet-blue with strong H_2SO_4.
129	—	*o*-Tolidine 	White scales. Resembles benzidine in its reactions. s.s. water; e.s. alcohol, ether. Primary amine. Forms a relatively insoluble sulphate, and gives a colour change with dilute Br-water, as described under benzidine. Diacetyl derivative, M.P. 306°. Dibenzylidene-tolidine, M.P. 150°, is obtained similarly to the benzidine compound, see Benzidine (M.P. 127°).
131	—	Dianisidine 	White plates, becoming violet on exposure to air. s. hot water; e.s. alcohol, ether. Primary amine. Sulphate is sparingly soluble in water. Diacetyl derivative, M.P. 235°. Chromate, brown, precipitated by the addition of chromic acid to saturated aqueous solution.

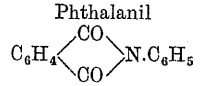
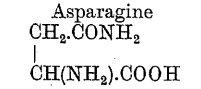
Properties of Solid Substances—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
132	—	β-Acetnaphthalide $C_{10}H_7.NH.COCH_3$	Colourless leaflets. s.s. hot water; e.s. alcohol, ether. Hydrolysed with HCl yields acetic acid and β-Naphthylamine. With Br in glacial acetic acid, yields monobrom-derivative, M.P. 140°.
134	—	Phenacetine p-$C_2H_5O.C_6H_4.NH.COCH_3$	Colourless plates. Odourless. s.s. hot water; e.s. alcohol. Hydrolysed with HCl yields acetic acid and p-ethoxy-aminobenzene (p-phenetidine), B.P. 254°. Readily nitrated on boiling with one part of HNO_3 and four parts of water, yielding o-nitrophenacetine in yellow needles, M.P. 103°.
140	267	p-Phenylenediamine $C_6H_4(NH_2)_2$	Colourless, but soon becoming discoloured on exposure. e.s. water, alcohol, ether. A very little of the base dissolved in water gives with $FeCl_3$ a green colour, rapidly turning brown. Primary amine. Diacetyl derivative, M.P. 299°. Dibenzoyl derivative, M.P. 305°.
142	—	o-Benzotoluidide $CH_3.C_6H_4.NH.COC_6H_5$	Colourless, odourless crystals. Almost i.s. water; e.s. alcohol, ether. Hydrolysed with 50 per cent. H_2SO_4 gives benzoic acid and o-toluidine.
144	—	o-Aminobenzoic Acid Anthranilic Acid $NH_2.C_6H_4.COOH$	Colourless, odourless needles. s.s. cold water, benzene; e.s. alcohol, ether. Amphoteric. Heated in dry tube decomposes, yielding a little aniline and CO_2. Ethyl ester, B.P. 267°. Hydrochloride, M.P. 193°. Acetyl derivative, M.P. 185°. Benzoyl derivative, M.P. 185°. Picryl derivative (obtained from Picryl Chloride, precipitated in hot alcoholic solution), M.P. 270°.

Properties of Solid Substances—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
146	307	Acet-*p*-Toluidide $CH_3.C_6H_4.NHCOCH_3$	Colourless, odourless crystals. Almost i.s. water; e.s. alcohol. Gives carbylamine reaction. Hydrolysed with HCl gives *p*-toluidine and acetic acid.
155	—	Benzo-*p*-Toluidide $CH_3.C_6H_4.NH.COC_6H_5$	Colourless, odourless crystals. i.s. water; e.s. alcohol. Gives carbylamine reaction. Hydrolysed with 50 per cent. H_2SO_4 to *p*-toluidine and benzoic acid.
159	—	Acet-*α*-naphthalide $C_{10}H_7.NH.COCH_3$	Colourless, odourless crystals. s.s. hot water; e.s. alcohol. Hydrolysed with HCl to *α*-naphthylamine and acetic acid.
160	—	Benzanilide $C_6H_5.NH.COC_6H_5$	Colourless, odourless crystals. i.s. water; e.s. alcohol. Gives carbylamine reaction. Hydrolysed with 50 per cent. H_2SO_4 gives benzoic acid and aniline.
170	—	*o*-Aminophenol $HO.C_6H_4.NH_2$	Colourless, odourless crystals, rapidly becoming discoloured in air. s. water, alcohol, ether. Primary amine. Dibenzoyl derivative, M.P. 182°.
173	360 *d.*	Michler's Ketone $C_6H_4.N(CH_3)_2$ | *p.p.*-CO | $C_6H_4.N(CH_3)_2$	Lustrous plates, almost i.s. water; e.s. alcohol. Tertiary amine. Gives ketone reactions. Fused with NH_4Cl and $ZnCl_2$ at 150–170° gives yellow mass (Auramine). Picrate, precipitated from alcoholic solution, M.P. 156°.
174	—	*m*-Aminobenzoic Acid $NH_2.C_6H_4.COOH$	Colourless plates, tending to discolour on exposure. m.s. water, alcohol, ether. Primary amine. Amphoteric. The saturated aqueous solution develops an orange colour on the addition of a solution of bleaching powder. Acetyl derivative, M.P. 248° *d.* Picryl derivative, from Picryl Chloride, precipitated in hot alcoholic solution, M.P. 233°. Ethyl ester, B.P. 294°.

Properties of Solid Substances—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
184 *d.*	—	*p*-Aminophenol $HO.C_6H_4.NH_2$	Colourless scales that are very readily oxidised by exposure. s. in water, alcohol. Primary amine. Its solutions in alkalies are coloured violet by atmospheric oxidation. Diacetyl derivative, M.P. 150°. Dibenzoyl derivative, M.P. 231°.
184 *d.*	—	*p*-Aminobenzoic Acid $NH_2.C_6H_4.COOH$	Colourless, odourless needles. s.s. water; e.s. alcohol, ether. Amphoteric. Primary amine. Benzoyl derivative, M.P. 278°. Picryl derivative, from Picryl Chloride precipitated in hot alcoholic solution, M.P. 285°. Ethyl ester, M.P. 89°. Methyl ester, M.P. 112°.
187	—	Hippuric Acid Benzoylglycine $C_6H_5CO.HN.CH_2.COOH$	Colourless, odourless needles. e.s. hot water, alcohol. i.s. benzene. Amphoteric. Hydrolysis with acids yields benzoic acid and glycine. Methyl ester, M.P. 80°. Ethyl ester, M.P. 60°.
203	—	Phthalanil 	Colourless needles. Sublimes. i.s. water; s. alcohol. Hydrolysed with HCl yields phthalic acid and aniline.
226 *d.* in sealed tube.	—	Asparagine 	See page 220.
233 *d.*	—	Glycine Glycocoll Aminoacetic Acid $CH_2.NH_2.COOH$	Colourless, odourless crystals. Neutral in reaction. Amphoteric. e.s. water; i.s. absolute alcohol, ether. Red colour with $FeCl_3$ solution. Boiled with CuO, filtered hot and cooled, yields bright blue needles of the Cu salt. Picrate, precipitated in aqueous solution by saturated alcoholic solution of picric acid, has M.P. 200°. Benzoylation gives hippuric acid, M.P. 187°.

Properties of Solid Substances—*continued.*

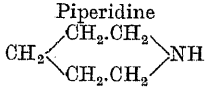
M.P. °C.	B.P. °C.	Name.	Characteristics.
234	—	Dimethylglyoxime (Nickel Reagent) $CH_3.C = NOH$ | $CH_3C = NOH$	Colourless, odourless crystals. i.s. water; e.s. alcohol, methyl alcohol, ether. When added in dilute alcoholic solution to a dilute solution of a nickel salt in faintly ammoniacal solution gives a flocculent red precipitate of nickel dimethylglyoxime.
236	—	Carbanilide Diphenylurea $OC:(NHC_6H_5)_2$	Colourless, odourless needles. v.s.s. water; e.s. alcohol, ether. Gives carbylamine reaction. Hydrolysed with HCl yields aniline and CO_2. Heated with acetic anhydride gives acetanilide and CO_2. In alcoholic solution Br precipitates the brom-derivative.
238	351	Carbazole C_6H_4 | C_6H_4 >NH	Colourless crystals, with faint odour. Very stable. i.s. water; s.s. alcohol, toluene. Fused with oxalic acid gives blue mass. Nitroso-compound, M.P. 82°. Benzoyl derivative, M.P. 96°. Picrate precipitated from solution in hot toluene gives M.P. 181°.
245	320	Oxanilide $CO.NH.C_6H_5$ | $CO.NH.C_6H_5$	Colourless crystals. i.s. water, ether; v.s.s. alcohol. Gives carbylamine reaction. Hydrolysed with HCl yields oxalic acid and aniline.
290 *d.* in sealed tube.	—	Aspartic Acid $CH_2.COOH$ | $CH.NH_2.COOH$	Colourless, odourless needles. Optically active. Soluble in hot water; i.s. alcohol. Amphoteric. Primary amine. Dextrorotatory in acid solution. Lævorotatory in alkaline solution. With HNO_2 yields malic acid.

332. Properties of Liquid Substances, containing C.H.[O].N only. The Amines, and related Compounds, which on Hydrolysis yield Amines.

For nitro-amines, see nitro-compounds, page 213. For the alkaloids and purines, see pages 242, 247.

B.P. °C.	Δ	Name.	Characteristics.
— 7°	—	Methylamine CH_3NH_2	Gas, intensely ammoniacal and fishy odour. Very soluble. Inflammable. Alkaline in reaction, but its solution will not redissolve $Ni(OH)_2$ as does NH_4OH. The hydrochloride, precipitated from its solution in dry ether, is deliquescent, M.P. 226°. Picrate, precipitated in strong aqueous solution, M.P. 215°. Chloroplatinate, M.P. 224°.
3	—	Trimethylamine $(CH_3)_3N$	Gas, ammoniacal, fishy odour. Very soluble in water. Alkaline in reaction. Hydrochloride, M.P. 270° *d.* Picrate precipitated from strong aqueous solution, M.P. 215°. Chloroplatinate, M.P. 242°.
7	—	Dimethylamine $(CH_3)_2NH$	Gas, ammoniacal, fishy odour. Very soluble in water. Secondary amine. Nitroso-compound, B.P. 151°. Hydrochloride, M.P. 171°. Picrate precipitated from strong aqueous solution, M.P. 155°. Chloroplatinate, M.P. 206°. Benzene sulphonamide, M.P. 47°.
19	0·689 (15°)	Ethylamine $C_2H_5NH_2$	Ammoniacal, fishy odour. Miscible with water. Alkaline in reaction. Hydrochloride, M.P. 76°. Picrate, M.P. 165°. Benzoyl derivative, M.P. 71°.
55	0·712 (15°)	Diethylamine $(C_2H_5)_2.NH$	Ammoniacal, fishy odour. v.s. water. Hydrochloride, M.P. 215°. Nitroso-derivative, B.P. 177°. Benzoyl derivative, B.P. 280°.
89	0·733 (15°)	Triethylamine $(C_2H_5)_3.N$	Ammoniacal odour; m.s. water. Tertiary amine. Picrate, M.P. 170°.

Properties of Liquid Substances—*continued.*

B.P. °C.	Δ	Name.	Characteristics.
105	0·861 (20°)	Piperidine 	Unpleasant, ammoniacal odour. Fumes in air. Alkaline in reaction. Miscible with water, alcohol. Secondary amine. Hydrochloride, M.P. 237°. Benzoyl derivative, M.P. 48°. Picrate, from solution in water, M.P. 145° *d.* Nitroso-derivative, yellow oil, decomposed on boiling.
115	0·989 (15°)	Pyridine $C_5H_5.N$	Characteristic, persistent odour. Miscible with water, alcohol, ether. Hygroscopic. Warmed with CH_3I, yields quaternary compound, M.P. 117°. Picrate, yellow needles, M.P. 163°.
184	1·025 (15°)	Aniline $C_6H_5.NH_2$	Colourless oil, darkens in air. Peculiar odour. Primary amine. s.s. water; miscible with alcohol, ether. Dilute aqueous solution gives purple colour with solution of bleaching powder. Hydrochloride, M.P. 198°. Acetyl derivative, M.P. 113°. Benzoyl derivative, M.P. 160°.
184	0·980 (23°)	Benzylamine $C_6H_5.CH_2.NH_2$	Strongly ammoniacal odour. Primary amine. Soluble in water and alcohol. Absorbs CO_2 and moisture from the air, forming the solid carbonate. Hydrochloride, M.P. 148°. Acetyl compound, M.P. 60°. Benzoyl derivative, M.P. 105°. Oxalate, 176° *d.*
193	0·958 (20°)	Dimethylaniline $C_6H_5.N(CH_3)_2$	Characteristic odour. Discolours on keeping. Almost i.s. water; e.s. alcohol, ether. Tertiary amine, but reacts in HCl solution with ice-cold $NaNO_2$, solution yielding the yellow hydrochloride of the *p*-nitroso-derivative, which on the addition of alkali and extraction with ether, yields the dark green *p*-nitrosodimethylaniline, M.P. 85°. Heated with four parts benzaldehyde and a little anhydrous $ZnCl_2$ over a very small flame, forms on cooling and acidification an intensely green solution (distinction from methylaniline).
195	0·987 (20°)	Methylaniline $C_6H_5.NH.CH_3$	Characteristic odour. Discolours on keeping. Almost i.s. water. Secondary amine. With HNO_2 gives an oily nitrosamine. Acetyl compound, M.P. 102°. Benzoyl derivative, 59°.

Properties of Liquid Substances—*continued.*

B.P. °C.	Δ	Name.	Characteristics.
199	1·003 (15°)	*o*-Toluidine $CH_3.C_6H_4.NH_2$	Odour like aniline. Darkens on exposure. Almost i.s. water. Primary amine. Acetyl derivative, M.P. 110°. Benzoyl derivative, M.P. 142°. Hydrochloride, M.P. 214°.
203	0·989 (20°)	*m*-Toluidine $CH_3.C_6H_4.NH_2$	Odour like aniline. Darkens on exposure. Almost i.s. water. Primary amine. Acetyl derivative, M.P. 65°. Benzoyl derivative, M.P. 125°. Hydrochloride, M.P. 225°.
205	0·963 (20°)	Ethylaniline $C_6H_5.NH.C_2H_5$	Odour like aniline. Darkens on exposure. Almost i.s. water. Secondary amine, forming a nitroso-derivative as a yellow oil. Acetyl derivative, M.P. 54°. Benzoyl derivative, M.P. 59°. Hydrochloride, M.P. 176°.
212	0·918 (15°)	*m*-Xylidine (1·3-dimethyl-4-aminobenzene) $(CH_3)_2.C_6H_3.NH_2$	Oily liquid, faint odour, darkens on exposure. Almost i.s. water. Primary amine. Acetyl derivative, M.P. 127°. Benzoyl derivative, M.P. 192°.
216	0·935 (20°)	Diethylaniline $C_5H_5.N(C_2H_5)_2$	Characteristic odour. Darkens on exposure. Almost i.s. water. Tertiary amine, but reacts with nitrous acid similarly to dimethylaniline, B.P. 193°, yielding a *p*-nitroso-compound, M.P. 84°. Heat with fused $ZnCl_2$ over a small flame, gives a blue or purple colour.
218	—	*p*-Xylidine (1·4-dimethyl-2-aminobenzene) $(CH_3)_2.C_6H_3.NH_2$	Faint odour. Darkens on exposure. Almost i.s. water. Primary amine, M.P. 15°. Acetyl derivative, M.P. 137°. Hydrochloride, M.P. 228°.
224	1·098 (15°)	*o*-Anisidine $NH_2.C_6H_4.OCH_3$	Faint odour. Almost i.s. water. Primary amine. Acetyl derivative, M.P. 84°. Benzoyl derivative, M.P. 64°.
228	—	*o*-Phenetidine $NH_2.C_6H_4.OC_2H_5$	Faint odour. v.s.s. water. Primary amine. Acetyl derivative, M.P. 80°.

Properties of Liquid Substances—*continued.*

B.P. °C.	Δ	Name.	Characteristics.
236	1·095 (20°)	Quinoline $C_9H_7.N$	Strong, characteristic odour. Darkens on keeping. s.s. water. Miscible with alcohol, ether. Tertiary amine. Reacts readily with CH_3I, forming a methiodide with M.P. 134°. Hydrochloride, M.P. 93°. Picrate, M.P. 203°.
240	1·099 (20°)	*iso*-Quinoline $C_9H_7.N$	M.P. 24°, but supercools. Tertiary amine. s.s. water; miscible with alcohol. Methiodide formed easily, M.P. 158°. Picrate, M.P. 223°.
243 *d.*	1·098 (22°)	Phenyl Hydrazine $C_6H_5.NHNH_2$	Darkens readily on exposure. s.s. water; miscible with alcohol, ether. Reduces Tollen's reagent and Fehling's solution in the cold with evolution of N_2. Benzaldehyde phenylhydrazone, M.P. 155°, readily formed.
254	1·061 (15°)	*p*-Phenetidine $NH_2.C_6H_4.OC_2H_5$	Faint odour. Darkens on exposure to air. Almost i.s. water; e.s. alcohol. Primary amine. Acetyl derivative (phenacetine), M.P. 134°. Benzoyl derivative, M.P. 173°.
267	> 1·0	Ethyl Anthranilate *o*-$NH_2.C_6H_4.COOC_2H_5$	Faint odour. Carbylamine reaction not readily given. s.s. water; e.s. alcohol. Hydrolysis with acid gives anthranilic acid (amphoteric) and ethyl alcohol. Acetyl derivative, M.P. 61°.
294	—	Ethyl *m*-Aminobenzoate *m*-$NH_2.C_6H_4.COOC_2H_5$	Primary amine. s.s. water; e.s. alcohol. Hydrolysis with HCl gives *m*-aminobenzoic acid (amphoteric) and ethyl alcohol. Benzoyl derivative, M.P. 113°.
298	1·067 (15°)	Benzylaniline $C_6H_5.NH.CH_2.C_6H_5$	M.P. 32°. Readily supercools. Secondary amine. Almost i.s. water; e.s. alcohol. Nitroso-compound, M.P. 58°. Hydrochloride, M.P. 197°. Benzoyl derivative, M.P. 104°.

THE IDENTIFICATION OF COMPOUNDS YIELDING ALDEHYDES AND KETONES ON HYDROLYSIS. OXIMES AND HYDRAZONES, ETC.

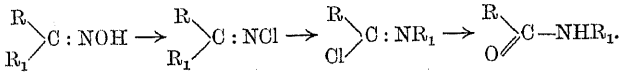
333. General Remarks.—The aldehyde or ketone produced by the acid hydrolysis of these compounds should be separated by distillation, filtration, or by extraction with ether, and may then be identified. The hydroxylamine, simultaneously produced from oximes, and the hydrazines derived from the hydrazones, may then be detected in the acid solution on account of the marked reducing properties of these substances towards Tollen's reagent or Fehling's solution. In carrying out this test it is best to evaporate the acid solution to dryness, and then redissolve the residue in a little distilled water before the addition of the test solution. Semicarbazide, produced by the hydrolysis of the semicarbazones, will also give a positive reaction.

The hydrolysis of these compounds is best effected by refluxing with pure concentrated hydrochloric acid.

Many oximes are soluble not only in acids, but also in caustic alkalies, although insoluble in solutions of the alkali carbonates. Aldoximes with phosphorus pentoxide yield nitriles :

$$R.CH:NOH + PCl_5 \longrightarrow R.C:N + POCl_3 + 2HCl$$

These nitriles may be extracted with ether and identified. On the other hand, ketoximes yield substituted amides on treatment with phosphorus pentachloride, and afterwards with water.



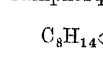
334. Properties of Solid Compounds containing C.H.[O].N only, which yield Aldehydes or Ketones on Hydrolysis. Oximes, Hydrazones, etc.

M.P. °C.	B.P. °C.	Name.	Characteristics.
33	118°/10 mm.	α-Benzaldoxime (Anti-) $C_6H_5.CH$ ‖ $HO.N$	Colourless needles. Faint odour. s.s. water ; e.s. alcohol, ether, benzene. Hydrolysis yields hydroxylamine and benzaldehyde. Treated with PCl_5, or on boiling with acetic anhydride, yields benzonitrile.

Properties of Solid Compounds—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
47	114	α-Acetaldoxime (Anti-) $CH_3.CH$ $\|\|$ $HO.N$	Colourless needles. v.s. water, alcohol, ether. Hydrolysis yields hydroxylamine and acetaldehyde.
59	135	Acetoneoxime $(CH_3)_2.C : NOH$	Colourless needles. Faint odour. v.s. water, alcohol, ether. Hydrolysis yields acetone and hydroxylamine.
105	—	Acetophenonephenylhydrazone CH_3 C_6H_5 $>C : N.NH.C_6H_5$	Colourless needles. Odourless. s.s. water, cold alcohol; e.s. ether. Hydrolysis yields acetophenone and phenylhydrazine.
109	—	α-Nitroso-β-Naphthol $C_{10}H_6.(OH).NO$ (Cobalt Reagent)	Brown crystals, tautomeric with β-Naphthoquinoneoxime. Hydrolysis yields hydroxylamine and β-Naphthoquinone. For tests, see nitroso-compounds, page 208.
119	—	Camphoroxime C_8H_{14} $<$ CH_2 / $C : NOH$	Colourless needles with pronounced odour of camphor. i.s. water; e.s. alcohol, ether. Only hydrolysed with great difficulty. Optically active.
120–130 *d.*	—	Quinonemonoxime *p*-Nitrosophenol $HO.C_6H_4.NO$	Yellowish needles. For tests, see nitroso-compounds, page 209.
129	—	β-Benzaldoxime (Syn-) $C_6H_5.CH$ $\|\|$ $N.OH$	Thin needles, colourless. s. alcohol, ether; v.d.s. benzene. Hydrolysis yields hydroxylamine and benzaldehyde. Shaken with cold dilute H_2SO_4 yields the α-isomer (anti-), M.P. 33°, page 56.
137	—	Benzophenonephenylhydrazone $(C_6H_5)_2.C : N.NHC_6H_5$	Odourless needles. i.s. water; s.s. alcohol. Hydrolysis yields benzophenone and phenylhydrazine.

Properties of Solid Compounds—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
141	—	Benzophenoneoxime $(C_6H_5)_2 : C : NOH$	Silky, odourless needles. Almost i.s. water; s. alcohol; v.s. ether. s. conc. HCl. Hydrolysis yields benzophenone and hydroxylamine. Treated with PCl_5 and then with water, yields benzanilide.
153	—	Camphorquinoneoxime 	Tautomeric with iso-nitrosocamphor. Colourless needles. i.s. water; s. alcohol, ether. Hydrolysis yields camphorquinone and hydroxylamine.
155	Distils without decomp.	α-Benzaldehydephenylhydrazone $C_6H_5.CH : N.NHC_6H_5$	Colourless, odourless prisms. Almost i.s. water; e.s. hot alcohol; s.s. ether. Hydrolysis yields benzaldehyde and phenylhydrazine. Boiled with acetic anhydride and one drop of conc. H_2SO_4, yields the β-isomer, M.P. 136°.
165	—	Benzophenonesemicarbazone $(C_6H_5)_2C : N.NH.CO.NH_2$	Colourless, odourless needles. Almost i.s. water; s. alcohol, acetone. Hydrolysis yields semicarbazide and benzophenone.

THE IDENTIFICATION OF THE ALKALOIDS

335. General Remarks.—The alkaloids, together with many other basic compounds, give a series of precipitates with a number of solutions that are termed "general alkaloidal reagents." It must be borne in mind that some of these reagents do not precipitate certain of the alkaloids, and, on the other hand, the formation of a precipitate does not necessarily prove the presence of an alkaloid.

The more important alkaloidal reagents are :

Picric Acid	This reagent, in saturated aqueous solution, is added to the alkaloid previously dissolved in water, or dilute hydrochloric acid, or in an organic solvent.	The M.P. of the resultant picrate, after recrystallisation, is of value in the identification.
Tannic Acid	This reagent, as a 10 per cent. aqueous solution, yields a whitish precipitate, usually soluble in dilute acids, or in an excess of the reagent.	
Mercuric Chloride	Yields with many alkaloids, well-defined double salts of definite M.P.	Many nitrogen compounds, apart from alkaloids, react thus.
Iodine in KI solution (Wagner's Reagent)	This solution is added to that of the alkaloid dissolved in dilute sulphuric acid. Brown amorphous precipitates are given.	
Mercuric Potassium Iodide (Mayer's Reagent)	Yields white or pale-coloured precipitates with solutions of the alkaloidal salts.	
Phosphomolybdic Acid (DeVry's Reagent)	May be added to the alkaloid in acid, or alcoholic solution.	Precipitates almost all basic organic compounds, the precipitates are insoluble in dilute acids, or in cold alcohol or ether.

Alkaloidal Reagents—*continued.*

Auric Chloride or Platinic Chloride	A 5–10 per cent. solution is added in slight excess to the alkaloid dissolved in dilute hydrochloric acid solution.	This precipitate is often of definite M.P., and is of particular value in the quantitative determination of the equivalent weight of the base.

Detailed particulars for the preparation of the above-mentioned alkaloidal precipitants are given on page 340, together with the test solutions mentioned hereafter.

As it is in practice often necessary to identify alkaloids present in *very small quantity*, a great many of the tests for this class of compound are colorimetric. Nearly all the alkaloids are, however, distinctly basic in character, soluble in dilute mineral acids, and precipitated by the addition of alkalies. Detailed tests are given in the following tables for the more common alkaloids only, as usually the advanced student is not required to establish their identification. The majority of natural alkaloids exhibit optical activity.

336. Properties of the Alkaloids.

M.P. °C.	Name.	Characteristics.
—	Coniine $C_8H_{17}N$	Liquid. B.P. 166°, with pronounced, unpleasant odour. s.s. water; e.s. alcohol, ether. Alkaline to phenolphthalein in aqueous alcoholic solution. Steam-volatile. Secondary amine. $\Delta = 0{\cdot}844$ (20°). $[\alpha]_D^{20} = +16°$. Hydrochloride, M.P. 217°. Platinichloride, M.P. 78°. Stirred with conc. H_2SO_4 and a crystal of $K_2Cr_2O_7$ gives a green colour.
—	Nicotine $C_{10}H_{14}N_2$	Liquid, usually brown in colour, B.P. 247°. Characteristic odour. Miscible with water, alcohol, ether. Steam-volatile. $\Delta = 1{\cdot}010$ (20°). $[\alpha]_D^{20} = -166{\cdot}4°$. Tertiary amine. Picrate, yellow needles, M.P. 219°. Platinichloride, 275° *d.* Alkaline in aqueous solution towards litmus but not to phenolphthalein. Stirred with conc. H_2SO_4 and a crystal of $K_2Cr_2O_7$ gives an olive-green colour.
80	*d. l*-Cocaine	See *l*-Cocaine (M.P. 98°).

Properties of the Alkaloids—*continued.*

M.P. °C.	Name.	Characteristics.
91	β-Eucaine $C_{15}H_{21}NO_2$	Synthetic local anæsthetic. Colourless crystals. e.s. ether, chloroform. Hydrochloride, M.P. 268°, only m.s. water (contrast Cocaine). Secondary amine. The precipitate with $KMnO_4$ soon turns brown.
98	*l*-**Cocaine** $C_{17}H_{21}NO_4$	Large colourless needles. v.s.s. water ; s. ether ; e.s. alcohol ; v.s. chloroform. $[\alpha]_D^{20} = -16°$ (in chloroform). Mydriatic. Solution of hydrochloride yields a purple precipitate of cocaine permanganate on the addition of dilute $KMnO_4$ solution. Heated with conc. H_2SO_4 and C_2H_5OH gives odour of ethyl benzoate. Hydrolysed at 100° with conc. H_2SO_4 yields benzoic acid, M.P. 120°. Hydrochloride, M.P. 186°, easily soluble in water (contrast β-Eucaine). The addition of a few drops of conc. HCl and a little $K_2Cr_2O_7$ solution yields a yellow-orange precipitate of cocaine chromate. $HgCl_2$ solution readily gives a white precipitate, M.P. 123°.
103	α-Eucaine $C_{18}H_{25}NO_4$	Synthetic local anæsthetic. Colourless crystals. e.s. alcohol, chloroform. Yields an immediate precipitate with 10 per cent. KI solution, unlike β-Eucaine and Cocaine. Yellow precipitate formed on adding $K_2Cr_2O_7$ to a solution of the hydrochloride. The precipitate with $KMnO_4$ soon turns brown. $HgCl_2$ solution readily gives a white precipitate (contrast β-Eucaine).
115	Atropine $C_{17}H_{23}NO_3$	Colourless needles. e.s. alcohol, chloroform ; m.s. ether ; s.s. hot water. Mydriatic. Evaporated to dryness on water-bath with a little fuming HNO_3 and the residue moistened with alcoholic KOH, gives a violet colour changing to red. Precipitates HgO (yellow) on warming with aqueous alcoholic $HgCl_2$. Picrate, yellow needles, M.P. 174°. Platinichloride, M.P. 207°. Aurichloride, M.P. 135°.
146	Papaverine $C_{20}H_{21}NO_4$	Colourless needles. Almost i.s. water ; s.s. ether ; e.s. alcohol, chloroform. Picrate precipitated with alcoholic picric acid, M.P. 180° *d.* Hydrochloride, M.P. 221° *d.* *Commercial specimens* on warming with conc. H_2SO_4 yield a violet solution, and with Froehde's reagent gives a green coloration, which turns blue and then red (due to the presence of a trace of kryptonine).

Properties of the Alkaloids—*continued.*

M.P. °C.	Name.	Characteristics.
155	Codeine $C_{18}H_{21}NO_3 + H_2O$	Methyl morphine. Colourless prisms. m.s. hot water; e.s. alcohol, chloroform. Alkaline in reaction to litmus. Lævorotatory. Froehde's reagent gives a green, then greenish-blue and ultimately a yellow coloration. Moistened with formalin, and then conc. H_2SO_4 added, a violet colour is given. Dissolved in H_2SO_4 gives a colourless solution, becoming blue on warming, or on the addition of $FeCl_3$. Picrate, M.P. 196° *d.* Hydrochloride, M.P. 264°.
170	Heroine Diacetylmorphine $C_{21}H_{23}NO_5$	Colourless crystals. Almost i.s. water; e.s. alcohol, ether. Is soluble in an excess of NH_4OH or of caustic alkalies. Froehde's reagent gives a purple colour, changing to blue, and ultimately yellow. Warmed with a mixture of H_2SO_4 in 3 parts of water and ethyl alcohol, gives the odour of ethyl acetate. Picrate precipitated from HCl solution gives M.P. 202° *d.*
173	**Quinine** $C_{20}H_{24}.N_2O_2$	$+ 3H_2O$, M.P. 57°, all the water is driven off at 130° Silky needles. v.s.s. water; e.s. alcohol, chloroform, ether. Strongly lævorotatory. In dilute *sulphuric acid* solution a marked blue fluorescence is shown. Dissolve a little of the base in dilute acetic acid; add Br- or Cl-water, and then NH_4OH—an intense emerald green solution is obtained (Thalleoquinine test). Stirred with strong H_2SO_4 and solid $K_2Cr_2O_7$ a green coloration is given. The hydrochloride, heated alone, gives off violet vapours resembling iodine.
176	Narcotine $C_{22}H_{23}NO_7$	Lustrous needles. Feebly basic. i.s. water; m.s. ether, alcohol; e.s. chloroform. Strongly lævorotatory in chloroform solution. Dextrorotatory in acid solution. Heated gently with one drop of H_2SO_4 and two drops of water on a crucible lid gives first an orange and ultimately an intense red-violet colour. Stirred with conc. H_2SO_4 and a crystal of $K_2Cr_2O_7$ an intense red coloration is given. Froehde's reagent gives a deep green colour. Picrate, M.P. 141°.
178	Brucine $C_{23}H_{26}N_2O_4$	$+4H_2O$ Hydrate has M.P. 105°. Colourless crystals. Almost i.s. water, ether; e.s. alcohol, chloroform. Strongly lævorotatory. Soluble in conc. HNO_3 with red colour. This solution heated on water bath changes to yellow: the addition of $SnCl_2$ at this stage yields an intense violet colour. With Froehde's reagent a pink colour is given, which changes to orange and ultimately to yellow. Erdmann's reagent gives a reddish colour, changing to orange and then to yellow. Picrate, M.P. 230° *d.*

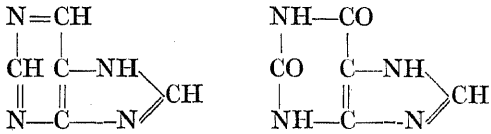
Properties of the Alkaloids—*continued.*

M.P. °C.	Name.	Characteristics.
212 *d.*	Adrenaline $C_9H_{13}NO_3$	Colourless needles. v.s.s. water, alcohol; i.s. chloroform; s.s. alkali, acid. Secondary amine. Lævorotatory. $FeCl_3$ in acid solution gives a green colour; in NaOH solution $FeCl_3$ gives an intense red colour. Reduces Tollen's reagent.
230	Caffeine	See Purines, page 247.
230 *d.*	**Morphine** $C_{17}H_{19}NO_3 + H_2O$	Colourless, odourless needles. v.s.s. hot water; s.s. hot alcohol and amyl alcohol. e.s. caustic alkalies. Lævorotatory. Alkaline in reaction. Soluble in pure HNO_3, giving an orange and then a yellow colour. One drop of *neutral* $FeCl_3$ added to a neutral solution of a morphine salt, or to the solid base on a white tile gives a dark blue colour. Dissolved in 0·5 c.c. conc. H_2SO_4 on a crucible lid and heated on the water bath for 10 minutes, cooled, and touched with a glass rod, moistened with dilute HNO_3, a deep red colour is given, which changes to orange. Acid solutions of morphine readily liberate iodine on the addition of iodic acid (characteristic test). Add one drop dilute $K_3Fe(CN)_6$ solution to a dilute solution of the alkaloid and then $FeCl_3$; an immediate precipitate of Prussian Blue is formed.
250 *d.*	Cinchonine $C_{19}H_{23}N_2O$	White, lustrous needles. Sublimes. Almost i.s. water; s.s. ether, chloroform; m.s. alcohol. Dextrorotatory. Resembles quinine in many of its reactions, but will not give the thalleoquinine test. Its salts are usually somewhat more soluble than the corresponding quinine salts and are not fluorescent in solution. $K_4Fe(CN)_6$ gives a yellow precipitate which is easily soluble in excess of the reagent (characteristic reaction). Picrate, yellow needles, from dilute acetic acid, M.P. 193°.
268 *d.*	**Strychnine** $C_{21}H_{22}N_2O_2$	Colourless prisms. Almost i.s. water; m.s. hot alcohol; e.s. chloroform. Soluble in conc. HNO_3, which on warming gives a yellow colour. Dissolved in conc. H_2SO_4 and stirred with a crystal of $K_2Cr_2O_7$, or better, a trace of MnO_2 scattered on surface, gives a violet, red, and ultimately an orange colour. With Mandelin's reagent gives a blue and then a violet colour, turning pink on the addition of NH_4OH. Picrate, yellow needles, M.P. 275–285° *d.*

THE IDENTIFICATION OF THE PURINES

337. General Remarks.—The purines in general give a positive result with the **Murexide Reaction** described as a general test in the table on page 202. The purines are colourless compounds of high melting-point.

The structures of the parent substance purine, and of xanthine, 2·6-dioxypurine, are represented by the formulæ:



from which the formulæ of the compounds in the table below can be easily written down.

M.P. °C.	Name.	Characteristics.
230	**Caffeine** (Theine) $C_8H_{10}N_4O_2 + H_2O$	1·3·7-trimethyl xanthine. Fine, colourless needles; e.s. hot water, chloroform; m.s. alcohol; s.s. ether. Feebly basic. Decomposed on boiling with concentrated alkalies yielding NH_3, $(CH_3)_3N$, etc. With $HgCl_2$ the double compound is slowly precipitated in white needles, M.P. 243° *d.* Evaporated with Cl- or Br-water, a trace of caffeine yields a brown residue which dissolves in NH_4OH giving a violet-red solution.
264	Theophylline $C_7H_8N_4O_2 + H_2O$	1 : 3 dimethyl xanthine. Colourless needles. Acid in reaction to phenolphthalein. s. hot water; m.s. hot alcohol, chloroform. Tannic acid precipitates the tannate, soluble in excess of the reagent. $AgNO_3$ precipitates Ag salt from solutions containing NH_4OH.
335 in sealed tube. Sublimes in open above 300	Theobromine $C_7H_8N_4O_2$	3 : 7-dimethyl xanthine. Minute, colourless crystals. v.s.s. hot water, hot chloroform. Almost i.s. other organic solvents. s. in acids and alkalies. Yields a crystalline precipitate in ammoniacal solution with $AgNO_3$, soluble in boiling water.

M.P. °C.	Name.	Characteristics.
—	**Uric Acid** $C_5H_4N_4O_3$	2·6·8-trioxypurine. Unchanged on heating to 360°. Crystalline powder. v.s.s. hot water; almost i.s. cold water, alcohol, ether. s. in alkalies and alkaline carbonates. Acid in reaction. A solution in Na_2CO_3 added to filter-paper moistened with $AgNO_3$ gives an immediate black stain of Ag. Heated alone evolves NH_3 and other products. Reduces Tollen's reagent.
—	Xanthine $C_5H_4N_4O_2$	2·6-dioxypurine. Unchanged at 360°. Crystalline powder. Almost i.s. water, alcohol, ether. v.s. alkali, but precipitated by CO_2. Soluble in conc. H_2SO_4 and not precipitated on dilution. $AgNO_3$ yields gelatinous precipitate in ammoniacal solution. $HgCl_2$ precipitates double compound from hot water solution, or from solution in ammonia. Treated on crucible lid with bleaching powder and NaOH solution, gives a dark green mass, changing to brown.
—	Guanine $C_5H_5N_5O$	2-Amino-6-oxypurine. Unchanged at 360°. Amorphous powder. i.s. water, alcohol, ether. e.s. alkalies and dilute mineral acids. $K_2Cr_2O_7$ solution gives precipitate with dilute acid solution. $K_4Fe(CN)_6$ solution gives brown precipitate in dilute acid solution. Picrate, formed from acid solution, gives M.P. 190°.

THE IDENTIFICATION OF COMPOUNDS CONTAINING C.H.[O].N AND HALOGEN

345. General Remarks.—The tests given in the following table are usually amply sufficient to demonstrate the nature of an organic substance containing both nitrogen and halogen. The properties of the more common of these substances are given in detail in the tables that follow :—

		PAGE
N and Cl	Solid compounds . .	251
	Liquid ,, . .	253
N and Br	Solid ,, . .	254
	Liquid ,, . .	255
N and I	Solid ,, . .	255

Salts of aromatic or aliphatic bases must be treated with an excess of alkali and the liberated amine identified by the tests given on pages 226–238.

TABLE X

Compounds containing C.H.[O].N and Halogen

Test.	Observation.	Deduction.	Example.
Odour of vapour.	Penetrating, lachrymatory.	Aromatic compounds, halogen substituted *in the side chain.*	Nitrobenzyl chlorides.
		Acid halides .	Nitrobenzoyl halides.
		Aliphatic chlornitrohydrocarbons and chloramines.	Chlorpicrin.
Warm the substance with distilled water.	Appreciably soluble and acid in reaction, effervescing on the addition of $NaHCO_3$.	Halide salts of aromatic bases.	Aniline hydrochloride.
		Some chlornitro-acids and acid chlorides, etc.	Chlornitrobenzoic acids.
		Chloramino-acids.	Chloraminobenzoic acids.
	Not acid in reaction.	Halide salts of aliphatic bases.	Methylamine hydrochloride.
Filter, and add a little HNO_3 and then $AgNO_3$.	Precipitate of silver halide shows very reactive halogen atom, or a salt of a base.	Halide salts of aromatic and aliphatic bases.	Amine hydrochlorides
		Acid chlorides .	Nitrobenzoyl chlorides.

Table X.—*continued.*

Test.	Observation.	Deduction.	Example.
Add NaOH solution and warm. If insoluble in water add alcohol.	NH_3 readily evolved.	Ammonium salts of halogen substituted acids.	
	NH_3 evolved on heating.	Halogen substituted amides.	Chloracetamide.
	Volatile amines evolved on heating.	Salts of aliphatic amines.	Methylamine hydrochloride.
	Oily base liberated soluble in excess of acid.	Salts of aromatic bases.	Aniline hydrochloride.
Filter, acidify with HNO_3 and add $AgNO_3$.	Precipitate of silver halide, shows reactive halogen atom.	Salts of aliphatic and aromatic bases.	Amine hydrochlorides.
		Acid chlorides .	Nitrobenzoyl chlorides.
		Aromatic compounds, halogen substituted in the side chain.	Nitrobenzyl chlorides.
		Aromatic compounds, halogen substituted in the nucleus, and also probably containing at least two nitro, or amino groups in the ortho- or para-position.	Chlordinitrobenzene.
			Picryl chloride.
If relatively insoluble in cold water, treat with cold dilute NaOH.	Soluble in alkali .	Halogen substituted nitro- and amino - acids, etc.	Nitrochlorbenzoic acids.
		Halogen substituted nitrophenols.	Chlornitro-phenols.
If relatively insoluble in cold water, treat with dilute HCl.	Soluble in acid .	Halogen substituted amines.	Chloraniline.
Test for the presence of an aromatic nitro-group by the test given on page 199.	Positive reaction .	Halogen substituted aromatic nitro-compound.	Chlornitro-acid, hydrocarbon, etc.
Test for an amino-group by the test given on page 201.	Positive reaction .	Halogen substituted amine or halide salt of an amine.	Chloraniline. Aniline hydrochloride.

346. Properties of Solid Compounds containing C.H.[O].N.Cl.

M.P. °C.	B.P. °C.	Name.	Characteristics.
32	243	*o*-Chlornitrobenzene $Cl.C_6H_4.NO_2$	Colourless crystals. Almost i.s. water; e.s. alcohol. Refluxed with Na in alcohol slowly yields *o*-nitrophenol. Reduction with Sn and HCl gives *o*-chloraniline, B.P. 207°.
35	—	*m*-Nitrobenzoyl Chloride $NO_2.C_6H_4.COCl$	Colourless crystals. Acid chloride. With alkali gives *m*-nitrobenzoic acid. Reduction with Sn and HCl gives *m*-amidobenzoic acid. Amide, M.P. 141°.
39	—	5-Chlor-2-nitrophenol $Cl.C_6H_3.(NO_2).OH$	Yellow crystals. m.s. hot water; e.s. alcohol. Soluble in alkalies with intense red colour.
44	235	*m*-Chlornitrobenzene $Cl.C_6H_4.NO_2$	Colourless. e.s. hot alcohol, ether. Reduced with Sn and HCl gives *m*-Chloraniline. Does not react with alcoholic KOH.
46	—	*m*-Nitrobenzyl Chloride $NO_2.C_6H_4.CH_2Cl$	Colourless crystals. Steam-volatile. e.s. alcohol. With alkaline $KMnO_4$ gives *m*-nitrobenzoic acid. With NaOH gives *m*-nitrobenzyl alcohol.
48	—	*o*-Nitrobenzyl Chloride $NO_2.C_6H_4.CH_2Cl$	Oxidised with alkaline $KMnO_4$ yields *o*-nitrobenzoic acid. With NaOH gives *o*-nitrobenzyl alcohol.
50	315 *d.*	Chlor-2-4-dinitrobenzene $Cl.C_6H_3.(NO_2)_2$	Colourless crystals. With alcoholic potash yields 2 : 4-dinitrophenol.
56	—	β-Chlor-α-naphthylamine $Cl.C_{10}H_6.NH_2$	Disagreeable odour. Steam-volatile. Primary amine. s.s. hot water; e.s. alcohol.
59	—	α-Chlor-β-Naphthylamine $Cl.C_{10}H_6.NH_2$	Primary amine. e.s. alcohol. Hydrochloride only sparingly soluble in cold water.
63	245	2·4-Dichloraniline $NH_2.C_6H_3.Cl_2$	Primary amine. e.s. alcohol, acids. Heated alcoholic KOH gives some ammonia and KCl. Benzoyl derivative, M.P. 115°.

Properties of Solid Compounds—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
70	232	*p*-Chloraniline $Cl.C_6H_4.NH_2$	Primary amine. e.s. alcohol, acids. Sulphate and oxalate only sparingly soluble. Benzoyl derivative, M.P. 182°.
71	—	*p*-Nitrobenzyl Chloride $NO_2.C_6H_4.CH_2Cl$	e.s. alcohol. Halogen atom readily removed with alkali. Oxidation with alkaline $KMnO_4$ gives *p*-nitrobenzoic acid. Reduction with Sn and HCl gives *p*-toluidine.
75	—	*p*-Nitrobenzoyl Chloride $NO_2.C_6H_4.COCl$	Acid chloride. With alkalies yields *p*-nitrobenzoic acid. Reduction with Sn and HCl gives *p*-amidobenzoic acid.
83	242	*p*-Chlornitrobenzene $Cl.C_6H_4.NO_2$	Slowly attacked by sodium ethylate solution, yielding a red solution containing *p*-nitrophenol. Acid reduction gives *p*-chloraniline.
83	—	Picryl Chloride $s\text{-}Cl.C_6H_2.(NO_2)_3$	Yellow crystalline needles. Almost i.s. water; s.s. alcohol. Reactive halogen atom readily removed by alkalies yielding picric acid. Treated with strong NH_4OH yields picramide. Hot alcoholic solution of Picryl Chloride treated with aniline gives scarlet crystals of picryl aniline, M.P. 177°.
93	—	Quinoline Hydrochloride $C_9H_7N.HCl$	See Quinoline (page 238). v.s. water, alcohol. Acid in reaction.
118	225 *d.*	Choracetamide $CH_2Cl.CONH_2$	Thick needles; s. water, alcohol. Boiled with alkali yields NH_3 and reactive halogen atom removed.
121	—	Methylaniline Hydrochloride $C_6H_5.NH(CH_3).HCl$	v.s. water, chloroform, alcohol. Acid in reaction. See Methylaniline (page 236).
141	238	Trichloracetamide $CCl_3.CONH_2$	Needles. s.s. water; e.s. alcohol, ether. Halogen atoms removed and NH_3 obtained on boiling with alkali, chloroform being first obtained.

Properties of Solid Compounds—*continued.*

M.P. °C.	B.P. °C.	Name.	Characteristics.
171	—	Dimethylamine Hydrochloride $(CH_3)_2.NH.HCl$	e.s. water, alcohol, chloroform. See Dimethylamine (page 235).
179	—	4-Chlor-3-nitrobenzoic Acid $Cl.(NO_2).C_6H_3.COOH$	Colourless needles. e.s. hot water. Acid in reaction. Acid chloride, M.P. 51°. Amide, M.P. 156°.
192	—	Aniline Hydrochloride $C_6H_5.NH_2.HCl$	v.s. water, alcohol. Acid in reaction. See Aniline (page 236).
226	—	Methylamine Hydrochloride $CH_3.NH_2.HCl$	Deliquescent. e.s. alcohol; v.s.s. chloroform. See Methylamine (page 235).

347. Properties of Liquid Compounds containing C.H.[O].N.Cl.

B.P. °C.	Δ	Name.	Characteristics.
112	1·664 (15°)	Chlorpicrin $C.Cl_3.(NO_2)$	Powerfully lachrymatory. Almost i.s. water; v.s. alcohol. Reduced with Fe in acetic acid solution gives methylamine.
148	—	γ-Chlorpyridine $Cl.C_5H_4N$	Disagreeable odour. Somewhat unstable. m.s. water. Chloroplatinate, M.P. 202°.
149	—	β-Chlorpyridine $Cl.C_5H_4N$	Penetrating, disagreeable odour. Very stable. s.s. water; e.s. alcohol. Chloroplatinate, M.P. 168°. Picrate, from alcoholic solution, M.P. 134°.
166	1·205 (15°)	α-Chlorpyridine $Cl.C_5H_4.N$	Penetrating odour. s.s. water; e.s. alcohol. Boiled in alcoholic solution with $HgCl_2$ yields a white crystalline double salt.
207	1·213 (20°)	o-Chloraniline $Cl.C_6H_4.NH_2$	Primary amine. v.s.s. water; e.s. alcohol, acids. Not decomposed with aqueous alkalies. Acetyl derivative, M.P. 87°. Benzoyl derivative, M.P. 100°.
230	1·222 (15°)	m-Chloraniline $Cl.C_6H_4.NH_2$	Primary amine. v.s.s. water; e.s. alcohol, acids. Not decomposed by aqueous alkalies. Acetyl derivative, M.P. 72°. Benzoyl derivative, M.P. 118°.

348. Properties of Solid Compounds containing C.H.[O].N.Br.

M.P. °C.	B.P. °C.	Name.	Characteristics.
18	251	*m*-Bromaniline	See liquid compounds (page 255).
30	250	*o*-Bromaniline $Br.C_6H_4.NH_2$	Colourless crystals. Primary amine. Almost i.s. water; e.s. alcohol, acids. Acetyl compound, M.P. 99°. Benzoyl compound, M.P. 114°.
41	261	*o*-Bromnitrobenzene $Br.C_6H_4.NO_2$	Yellowish crystals. e.s. alcohol. Nitro-compound. Reduction with Sn and HCl gives *o*-Bromaniline, B.P. 250°, M.P. 30°. Refluxed with Na ethylate yields *o*-nitrophenol (red colour).
56	256	*m*-Bromnitrobenzene $Br.C_6H_4.NO_2$	Yellowish crystals. e.s. alcohol. Nitro-compound. Reduction with Sn and HCl yields *m*-bromaniline, B.P. 251°. Unattacked on refluxing with alcoholic KOH.
63	*d.*	*p*-Bromaniline $Br.C_6H_4.NH_2$	Colourless crystals. Primary amine. Almost i.s. water; e.s. alcohol, acids. Acetyl derivative, M.P. 165°. Benzoyl derivative, M.P. 202°.
66	—	"Neuronal" $(C_2H_5)_2.CBr.CONH_2$	Colourless crystalline powder. Distinct odour. s.s. cold water; e.s. alcohol. Boiled with water liberates HBr and gives a white crystalline product of M.P. 98°. Heated with alkalies, NH_3 is evolved, and the Br replaced.
106	—	*p*-Bromphenyl-hydrazine $Br.C_6H_4.NH.NH_2$	Colourless needles that darken on keeping, m.s. hot water; e.s. alcohol. Br not readily displaced. Powerful reducing agent. Reduces Tollen's reagent and Fehling's solution. Acetyl compound, M.P. 161°. Forms crystalline hydrazones with aldehydes and ketones.
126	255	*p*-Bromnitrobenzene $Br.C_6H_4.NO_2$	Yellowish crystals. s.s. water; e.s. alcohol. Nitro-compound. Reduction with Sn and HCl yields *p*-Bromaniline, M.P. 63°. Yields *p*-nitrophenol and solution becomes orange on refluxing with sodium ethylate.

349. Properties of Liquid Compounds containing C.H.[O].N.Br.

B.P. °C.	Name.	Characteristics.
251	*m*-Bromaniline $Br.C_6H_4.NH_2$	Almost colourless. Primary amine. Solidifies on cooling with ice, giving product of M.P. 18°. Almost i.s. water; e.s. alcohol, acids. Acetyl derivative, M.P. 87°. Benzoyl derivative, M.P. 120°.

350. Properties of Solid Compounds containing C.H.[O].N.I.

M.P. °C.	B.P. °C.	Name.	Characteristics.
25	—	*m*-Iodoaniline $I.C_6H_4.NH_2$	Colourless leaflets. Primary amine. e.s. alcohol, acids. Acetyl derivative, M.P. 119°.
34	280	*m*-Iodonitrobenzene $I.C_6H_4.NO_2$	Yellow needles. e.s. alcohol. Nitro-compound. Reduced with Sn and HCl gives *m*-Iodoaniline, M.P. 25°.
49	293	*o*-Iodonitrobenzene $I.C_6H_4.NO_2$	Yellow needles. e.s. alcohol. Nitro-compound. Acid reduction gives *o*-iodoaniline, M.P. 56°.
56	—	*o*-Iodoaniline $I.C_6H_4.NH_2$	Colourless needles. Unpleasant odour. Primary amine. Steam-volatile. e.s. alcohol, acids. Acetyl derivatives, M.P. 109°, easily sublimes.
62	—	*p*-Iodoaniline $I.C_6H_4.NH_2$	Compare *o*-isomer (M.P. 56°). Acetyl derivative, M.P. 182°.
Decomposes about 140°	—	"Iodol" Tetraiodopyrrole $I_4.C_4.NH$	Yellow crystalline powder. Odourless. Secondary amine. e.s. alcohol, acids. Soluble in H_2SO_4 with intense green colour. HNO_3 when added to alcoholic solution gives an intense red colour. (Odourless substitute for iodoform.)
171	—	*p*-Iodonitrobenzene $I.C_6H_4.NO_2$	Yellow needles. e.s. alcohol. Nitro-compound. Reduced with Sn and HCl gives *p*-Iodoaniline, M.P. 62°.

THE ANALYSIS OF COMPOUNDS CONTAINING C.H.[O].N.S OR C.H.[O].N.S AND HALOGEN

351. General Remarks.—The usual compounds that contain S as well as N belong to the following classes :—

(*a*) Sulphates of organic bases. *E.g.*, $C_6H_5 . NH_2 . H_2SO_4$.

(*b*) Nitro- or amino-sulphonic acids or acid chlorides. *E.g.*, $NH_2 . C_6H_4 . SO_3H$; $NO_2 . C_6H_4 . SO_2Cl$.

(*c*) Sulphonamides. *E.g.*, $C_{10}H_7 . SO_2NH_2$.

(*d*) Thioureas and thiocarbanilides. *E.g.*, $(C_6H_5 . NH)_2CS$.

(*e*) Thiocyanates, R . S . C ⋮ N, and *iso*-thiocyanates, R . N : C : S.

The tests given in the following scheme of analysis are usually sufficient to enable the nature of the substance to be determined.

TABLE XI

Compounds containing C.H.[O].N.S and Halogen

Test.	Observation.	Deduction.	Remarks.
Odour . .	Characteristic and Pungent (Mustard Oils).	*iso*-Thiocyanates .	Confirm by gently warming with ammoniacal $AgNO_3$, a black precipitate of Ag_2S is readily formed.
Solubility in water.	Soluble and strongly acid in reaction.	Sulphates of bases.	*E.g.*, $C_6H_5.NH_2.H_2SO_4$. Confirm by the addition of HCl and $BaCl_2$.
		Amino- or nitro-sulphonic acids.	*E.g.*, $NO_2.C_6H_4.SO_3H$.
	Not very soluble, but gives acidic reaction on heating, and the solution gives a precipitate of AgCl with $AgNO_3$.	Sulphonyl chlorides	*E.g.*, $NO_2.C_6H_4.SO_2Cl$.

Table XI.—*continued.*

Test.	Observation.	Deduction.	Remarks.
Warm with alcoholic NaOH.	Ammonia evolved.	Ammonium salts of sulphonic acids. Sulphonamides. Thioureas . .	Identify by examination of the liberated sulphonic acid. *E.g.*, $(NH_2)_2.CS$.
	Amines evolved or liberated.	Substituted sulphonamides and thioureas.	*E.g.*, $(C_6H_5NH)_2CS$.
Filter the cooled solution, dilute, acidify, and add a drop of $FeCl_3$.	Blood-red colour of ferric thiocyanate.	Thiocyanate .	*E.g.*, $C_6H_5.S.C:N$.
Fuse the compound, if not too volatile, with moistened NaOH or KOH for 5 minutes, cool, dissolve in water and acidify with HCl.	H_2S evolved .	From substances containing divalent S, such as the thioureas and the sulphides.	*E.g.*, $(C_6H_5.NH)_2CS$.
	SO_2 evolved .	From sulphonic acids, sulphonamides, sulphonyl halides, etc.	*E.g.*, $NO_2.C_6H_4.SO_3H$.
Add $BaCl_2$ to the resultant solution.	$BaSO_4$ precipitated.	In some few cases, such as sulphanilic acid, alkali fusion yields a sulphate and not a sulphite.	*E.g.*, $NH_2.C_6H_4.SO_3H$.
Test for aromatic nitro- and amino-groups by the tests given on pages 199–201.		The presence of nitro- or amino-groups suggests the compound to be a nitro- or amino-substituted sulphonic acid, acid chloride or amide.	Sulphonic acids may be identified by converting them to the corresponding sulphonyl chloride with PCl_5, and then to the sulphonamide as described in detail below (**352**).

352. The preparation of sulphonyl chlorides and sulphonamides from sulphonic acids is often necessary in order to complete the identification of these compounds. The dry sulphonic acid should be intimately mixed with an excess of phosphorus pentachloride, and then warmed gently to complete the reaction. The product is then treated with cold water to remove excess of phosphorus halides. A small quantity can be recrystallised, if it is a solid, from an inert solvent and a determination of the melting-point made.

The acid chloride thus produced can be converted into the corresponding sulphonamide by boiling with an excess of strong ammonia :

$$C_6H_5 . SO_2Cl + 2NH_3 \rightarrow C_6H_5 . SO_2NH_2 + NH_4Cl.$$

The sulphonamide obtained by partial or complete evaporation should be recrystallised from dilute alcohol.

Esters of sulphonic acids may be prepared by boiling the sulphonyl chloride and absolute methyl alcohol together, or by the Fischer process, employing absolute methyl or ethyl alcohol, the sulphonic acid, and dry hydrogen chloride, as described on page 73.

353. The Thiocyanates and Iso-thiocyanates.—In the case of the thiocyanates, which have the constitution R . S . C ⋮ N, reduction with metals in acid solution results in the formation of a mercaptan, or thiophenol, and hydrocyanic acid :

$$R . SCN + 2\dot{H} \rightarrow R . SH + HCN.$$

On the other hand, the iso-thiocyanates, R . N : C : S, are reduced by nascent hydrogen yielding primary amines, which are liberated with thioformaldehyde on the addition of alkali :

$$R . NCS + 4\dot{H} \rightarrow R . NH_2 + CH_2S.$$

The iso-thiocyanates have characteristic pungent, mustard-like odours, and are known as the *Mustard Oils*. With ammoniacal silver nitrate, a black precipitate of silver sulphide is readily produced on warming. Warmed with alcohol, and freshly precipitated yellow mercuric oxide, black mercuric sulphide is precipitated. Iso-thiocyanates may be identified by evaporating them with an excess of strong ammonia, whereby the thioureas are obtained :

$$R . NCS + NH_3 \rightarrow R . NH . CS . NH_2.$$

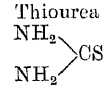
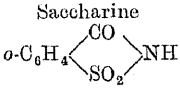
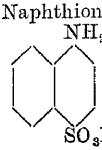
The mustard oils, on boiling with pure hydrochloric acid, are hydrolysed, yielding sulphuretted hydrogen and an amine :

$$R.NCS + 2H_2O \rightarrow R . NH_2 + CO_2 + H_2S.$$

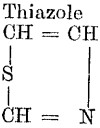
354. Properties of Solid Compounds containing C.H.[O].N.S only.

M.P. °C.	Name.	Characteristics.
41	Benzyl Thiocyanate $C_6H_5.CH_2.SCN$	Colourless prisms. B.P. 232°. Pungent odour. Almost i.s. water; e.s. alcohol. Oxidised with alkaline $KMnO_4$ gives benzoic acid.
107	1·3-Dinitro-4-benzene-sulphonic Acid $(NO_2)_2.C_6H_3.SO_3H+3H_2O$	Pale yellow needles. Deliquescent. e.s. water and alcohol. Boiled with aqueous alkalies gives 2·4-dinitrophenol, M.P. 114°. Acid chloride, M.P. 102°. Sulphonamide. M.P. 153°.
108	Thioacetamide $CH_3.CS.NH_2$	Colourless prisms. With faint odour of H_2S. v.s. water and alcohol. Boiled with aqueous NaOH yields sodium acetate, sodium sulphide and NH_3. Boiled with HCl yields H_2S.
126	Azobenzene-*p*-sulphonic Acid $C_6H_5.N:N.C_6H_4.SO_3H+3H_2O$	Dark orange crystals, strongly acid in reaction. m.s. water; s.s. alcohol. Basalt precipitated. Sulphonyl chloride, orange needles, M.P. 82°.
137	*p*-Toluenesulphonamide $CH_3.C_6H_4.SO_2NH_2$	Colourless leaflets. s.s. water; m.s. alcohol; e.s. caustic alkalies. Boiled with NaOH yields ammonia and *p*-Toluenesulphonic acid, M.P. 92°.
150	Benzenesulphonamide $C_6H_5.SO_2NH_2$	Colourless needles. m.s. hot water; e.s. alcohol and caustic alkalies. Boiled with NaOH yields ammonia and deliquescent benzenesulphonic acid, M.P. 65°, which yields a para-toluidide, M.P. 121°.
153	Thiocarbanilide $(C_6H_5NH)_2:CS$	Lustrous plates. Almost i.s. water. e.s. alcohol, alkalies. Reprecipitated from solution in NaOH with CO_2 or HCl. Distilled with conc. HCl, almost to dryness, yields a distillate containing phenyl mustard oil with characteristic odour. Boiled in alcoholic solution with freshly precipitated HgO and filtered hot, gives carbanilide, M.P. 236°. Gives carbylamine reaction faintly.

Properties of Solid Compounds—*continued.*

M.P. °C.	Name.	Characteristics.
154	Phenylthiourea $C_6H_5NH.CS.NH_2$	Colourless needles. e.s. hot water, alcohol, alkalies. Reprecipitated from solution in NaOH with CO_2 or HCl. Gives pronounced carbylamine reaction. Distilled with HCl yields pungent smelling phenyl mustard oil, like thiocarbanilide. Boiled with aniline yields thiocarbanilide.
159	Ammonium Thiocyanate $NH_4.SCN$	Deliquescent crystals, soluble in an equal volume of water with marked endothemic reaction. Colours $FeCl_3$ solution blood red, which colour is not discharged on boiling with HCl.
170–180	Thiourea 	Colourless needles. m.s. cold water; v.s.s. cold alcohol. Heated in a small tube just above its M.P. for 2 minutes, cooled and extracted with water, gives ammonium thiocyanate in solution which gives the characteristic reaction with $FeCl_3$. With neutral $KMnO_4$ solution, gives urea and H_2SO_4.
220	Saccharine 	Colourless crystalline powder. m.s. hot water, alcohol. Aqueous solution distinctly acid and intensely sweet. e.s. NaOH, Na_2CO_3 and NH_4OH solutions, and reprecipitated from these solutions by HCl. Fuse gently with NaOH moistened with water until no more NH_3 is evolved; dissolve residue in water, just neutralise with HCl, and test with $FeCl_3$. A violet colour, due to the presence of salicylic acid, is given.
Chars at 280–300 *d.*	Sulphanilic Acid p-$NH_2.C_6H_4.SO_3H + 2H_2O$	s.s. water, strongly acid in reaction. With Br-water in excess, the aqueous solution yields a copious yellow precipitate. Distilled with soda-lime gives aniline. Is a primary amine, which on diazotisation couples with β-naphthol in NaOH solution to give an orange dye, or with dimethylaniline in HCl solution to give methyl orange.
Chars.	Naphthionic Acid 	Colourless needles. s.s. hot water. Strongly acid in reaction. Primary amine. Soluble in acids and alkalies; the solutions of its salts are fluorescent. The corresponding sulphonamide has M.P. 206°, and yields with acetic anhydride an acetyl derivative, M.P. 241°.

355. Properties of Liquid Compounds containing C.H.[O].N.S only.

B.P. °C.	Δ	Name.	Characteristics.
117	1·202 (15°)	Thiazole 	Colourless liquid with odour of pyridine. Soluble in water. The picrate, precipitated from aqueous solution, has M.P. 150°.
130	1·069 (24°)	Methyl Thiocyanate $CH_3.SCN$	Colourless liquid with mild odour. i.s. water; miscible with alcohol. Heated with alcoholic KOH yields ammonia. See paragraph **353.**
131	1·003 (15°)	Ethyl Isothiocyanate $C_2H_5.NCS$	Colourless oil with pungent, mustard-like odour. Blisters the skin. See paragraph **353.**
144	1·007 (20°)	Ethyl Thiocyanate $C_2H_5.SCN$	Resembles the methyl ester (see above).
150	1·020 (15°)	Allyl Isothiocyanate $C_3H_5.NCS$	"Mustard Oil." Almost i.s. water; miscible with alcohol. See paragraph **353.**
221	1·138 (15°)	Phenyl Isothiocyanate $C_6H_5.NCS$	"Phenyl Mustard Oil." M.P. 153°. Almost i.s. water. Heated with aniline gives thiocarbanilide. See paragraph **353.**
230	1·156 (15°)	Phenyl Thiocyanate $C_6H_5.SCN$	Resembles the methyl ester (see above).

THE IDENTIFICATION OF COMPOUNDS CONTAINING C.H.[O].S AND HALOGEN ONLY

356. The great majority of compounds that contain only sulphur and halogen as " additional elements " belong to one of the following classes :—

(1) Halogen substituted sulphonic acids or sulphides, *e.g.*, *p*-chlorbenzenesulphonic acid, $Cl . C_6H_4 . SO_3H$; dichlordiethyl sulphide, $(CH_2 . Cl . CH_2)_2S$.

(2) Aromatic sulphonyl chlorides, *e.g.*, $C_6H_5 . SO_2Cl$.

The tests given in the following table are sufficient to distinguish these compounds.

TABLE XII

Compounds containing C.H.[O].S and Halogen

Test.	Observation.	Deduction.	Remarks.
Solubility in water.	(*a*) Soluble in cold water, with pronounced acidic reaction.	Halogen substituted sulphonic acids.	*E.g.*, chlorbenzene sulphonic acids. To identify prepare acid chloride and amide as given on page 258.
	(*b*) Decomposed by boiling water, forming a strongly acid solution, which on the addition of HNO_3 and $AgNO_3$ yields AgCl.	Sulphonyl Chlorides	*E.g.*, $C_6H_5.SO_2Cl$. To identify prepare corresponding sulphonamide as described on page 258.
Warm with aqueous NaOH, acidify with HNO_3, filter, and add $AgNO_3$ to the filtrate.	A precipitate of silver halide indicates the presence of an easily replaceable halogen atom.	Sulphonyl Chloride or Halogen substituted sulphide.	See above. *E.g.*, $(CH_2Cl.CH_2)_2S$.
	A faint precipitate of silver halide.	Probably a phenolsulphonic acid, containing halogen in the nucleus.	*E.g.*, $HO.C_6H_3.(Cl).SO_3H$.

Table XII.—*continued.*

Test.	Observation.	Deduction.	Remarks.
Boil with water, exactly neutralise with NaOH, filter and add $FeCl_3$ to the cold filtrate.	The formation of a blue or violet colour indicates the presence of a phenolic group.	Either a halogen phenol-sulphonic acid, or a derivative of a phenol-sulphonyl chloride.	*E.g.*, $HO.C_6H_3.(Cl).SO_3H$.
Fuse the compound, if not too volatile, with moistened NaOH or KOH for 5 minutes. Cool, dissolve in water and acidify with HCl.	H_2S evolved SO_2 evolved, or else $BaSO_4$ precipitated on addition of $BaCl_2$ to solution.	From substances containing divalent S. From sulphonic acids or their derivatives.	*E.g.*, Halogen substituted sulphides.

357. Properties of Solid Compounds containing C.H.[O].S and Halogen.

M.P. °C.	Name.	Characteristics.
53	*p*-Chlorbenzenesulphonyl Chloride $Cl.C_6H_4.SO_2Cl$	Colourless plates. Decomposed by boiling water to corresponding sulphonic acid, M.P. 68°. Sulphonamide, M.P. 143°.
67	*α*-Naphthalenesulphonyl Chloride $C_{10}H_7.SO_2Cl$	Colourless plates. e.s. alcohol, ether. On boiling with water gives corresponding acid, M.P. 85°. Sulphonamide, M.P. 149°. Methyl ester, M.P. 78°.
68	*p*-Chlorbenzenesulphonic Acid $Cl.C_6H_4.SO_3H$	Deliquescent, crystalline mass. Corresponding chloride, described above, M.P. 53°. Sulphonamide, M.P. 143°.
69	*p*-Toluenesulphonyl Chloride $CH_3.C_6H_4.SO_2Cl$	Colourless plates. e.s. ether. Decomposed on boiling with water, yielding the corresponding acid, M.P. 92°. Sulphonamide, M.P. 137°. Ethyl ester, M.P. 32°.
76	*β*-Naphthalenesulphonyl Chloride $C_{10}H_7\ SO_2Cl$	Colourless plates. m.s. ether. Decomposed on boiling with water, yielding the corresponding acid. Sulphonamide, M.P. 217°. Methyl ester, M.P. 56°.

358. Properties of Liquid Compounds containing C.H.[O].S and Halogen.

B.P. °C.	Name.	Characteristics.
217 *d.*	$\beta\cdot\beta^1$-Dichlordiethyl Sulphide $(CH_2.Cl.CH_2)_2.S$ "Mustard Gas"	Faint odour. Painful effect on the skin. Vapour very toxic. Steam-volatile. Almost i.s. water; e.s. alcohol, ether. Solidifies in ice, yielding long needles, having M.P. about 13°.
246 *d.*	Benzenesulphonyl Chloride $C_6H_5.SO_2Cl$	Colourless prisms. e.s. alcohol, ether. Decomposed by boiling water, giving corresponding acid, deliquescent, M.P. 65°. Sulphonamide, M.P. 150°. *p*-Toluidide, M.P. 121°.

THE SEPARATION OF MIXTURES OF ORGANIC COMPOUNDS

359. Before attempting the identification of the constituents of an organic mixture it is always necessary first to isolate each component in a state of purity.—The procedure to be adopted for separating the components of an organic mixture necessarily depends on the nature of the organic substances present. In many cases the separation may be made by taking advantage of the diverse chemical properties of the constituent compounds, whereas the separation of two members of an homologous series usually can only be effected by such physical processes as fractional distillation.

The separation of an organic mixture should be attempted as outlined in the schemes set out below. The separated components, after purification by distillation or crystallisation, should then be examined individually by the methods already described.

360. Separation of Mixtures by Fractional Distillation.—Should the mixture appear to contain a fairly volatile substance, separation by distillation should be first tried. The mixture should be distilled from a small flask, containing a thermometer, and the separate fractions collected in clean, dry test tubes. The flask should be heated either on a water bath or else directly with a small luminous flame. It should be remembered that the fractional distillation of liquids of moderately high boiling-point is complicated by the fact that many organic liquids form binary or ternary vapour mixtures.

361. Separation of Mixtures by Aqueous Acids and Alkalies.—The separation of organic substances of diverse chemical properties may often be effected by the judicious use of acids and alkalies as outlined in Table XIII.

362. Separation of Mixtures by Ether, Acids and Alkalies.—The separation of mixtures of organic compounds may often be effected in the following way (see Table XIV.), which is a modification of the method given in Table XIII.

363. In some cases the separation of mixtures of organic compounds may be effected by such processes as selective solution, steam distillation or fractional crystallisation.

Selective Solution.—The mixture is warmed with small quantities

of different solvents that may exert selective solution. The more usual solvents employed for this purpose are water, ether, alcohol, petroleum, ether, chloroform and glacial acetic acid. Separated products must always be recrystallised before proceeding with their identification.

364. Steam Distillation.—Simple distillation in steam is sometimes of great value as a process of separation, even for compounds of the same family, such as the isomeric ortho- and para-nitrophenols and the nitrotoluenes.

Steam Distillation from acid and alkaline media is of great value for the separation of steam-volatile neutral compounds from basic and acidic compounds, as well as for the separation of basic and acidic substances. The process of steam distillation usually gives a very sharp separation, but it must be remembered that *complex compounds may be hydrolysed in the process and thus the identity of the original substances destroyed.* The method usually applied for separation by steam distillation is shown in Table XV.

365. Fractional Crystallisation. Fractional Distillation under Reduced Pressure. Sublimation.—These processes of separation should not be applied to mixtures of organic compounds unless the methods previously described have failed to yield satisfactory results.

TABLE XIII

Separation of Mixtures by Acids and Alkalies

Thoroughly stir the mixture with an excess of dilute **HCl** and filter.

Filtrate contains basic constituents and water-soluble compounds. Add a slight excess of **NaOH** and filter.		**Residue** contains neutral and acidic compounds. Thoroughly stir with dilute **NaOH** and filter.			
Precipitate, solid or liquid, consists of relatively **insoluble basic compounds** such as the aromatic amines.	**Filtrate** may contain **easily soluble neutral compounds, or basic compounds readily soluble in water,** such as the aliphatic amines. Warm the solution and, (*a*) if ammoniacal vapours are evolved, distil and absorb the vapours in HCl; evaporate the acid solution to dryness. The residue contains the hydrochlorides of **aliphatic amines.** (*b*) If no ammoniacal vapours are evolved, just acidify with conc. HCl, extract with ether, evaporate, and examine the residue for **neutral, soluble compounds.**	**Residue** contains neutral compounds. Dissolve in ether and shake with saturated $NaHSO_3$ solution and separate.		**Filtrate** contains acidic compounds. Pass a rapid current of CO_2 through the filtrate for 2 minutes. Filter.	
		Ethereal Solution contains neutral compounds. Evaporate and examine residue for **alcohols, ethers, hydrocarbons, esters, nitriles,** etc.	**Aqueous Solution** contains carbonyl compounds. If a precipitate has formed, acidify and extract with ether, or filter to obtain **aldehydes and ketones.**	**Precipitate** contains insoluble pseudo-acidic compounds, such as **naphthols, phenols,** also substituted thioureas, etc.	**Filtrate** contains acidic substances. Acidify with HCl. Filter or extract with ether to obtain **acids, nitrophenols,** some sulphonamides and imides (saccharine).

TABLE XIV

Separation of Mixtures by Ether, Acids and Alkalies

The mixture is shaken vigorously in a separating funnel with excess of dry ether, and filtered.

Insoluble Residue contains **metallic salts of acids, carbohydrates, sulphonic acids,** and **salts of bases** such as aniline hydrochloride, etc.	**Ethereal Solution** is shaken in the separating funnel with successive quantities of (*a*) dilute H_2SO_4; (*b*) Na_2CO_3 solution; (*c*) dilute NaOH; (*d*) saturated $NaHSO_3$ solution.				
	H_2SO_4 extract contains basic compounds. Add excess of NaOH solution and obtain **amines** by separation or distillation.	**Na_2CO_3 extract** contains acidic compounds. Acidify and obtain **acids, nitrophenols,** and other acid compounds by filtration, distillation, or extraction with ether.	**NaOH extract** contains pseudo-acidic compounds, such as **phenols, naphthols,** which are liberated on the addition of acid.	**$NaHSO_3$ extract** contains **aldehydes** and **ketones.** If a precipitate has formed, acidify to liberate these compounds.	**Residual Ethereal Solution** contains neutral compounds, such as **ethers, alcohols, hydrocarbons, esters** and **nitriles.** These are obtained on evaporating off the ether.

TABLE XV

Separation of Mixtures by Steam Distillation

Add the mixture to an excess of dilute sulphuric acid and steam-distil.

<table>
<tr><td colspan="3">Non-volatile Residue contains basic compounds and non-volatile substances. Add excess of NaOH and steam-distil.</td><td colspan="2">Distillate contains volatile acidic and neutral compounds. Add excess of NaOH and steam-distil.</td></tr>
<tr><td rowspan="2">Distillate contains volatile basic compounds. If insoluble separate, or extract with ether. If soluble, add excess of HCl and evaporate to dryness to obtain the hydrochloride.</td><td colspan="2">Non-volatile Residue contains non-volatile basic, acidic or neutral compounds. Add a little H_2SO_4, extract with ether, and separate.</td><td rowspan="2">Distillate contains neutral steam-volatile compounds, which are obtained by separation or by extraction with ether.</td><td rowspan="2">Non-volatile residue contains volatile acidic compounds, which are liberated on acidification with H_2SO_4, and obtained by filtration, extraction with ether, or steam-distillation.</td></tr>
<tr><td>Ethereal Solution contains neutral or acidic non-volatile compounds, which are obtained on evaporating off the ether.</td><td>Acid Solution contains basic, non-volatile compounds, which are liberated on addition of NaOH.</td></tr>
</table>

SECTION IV

ULTIMATE ANALYSIS

375. General Remarks.—This section describes the general methods used for the ultimate analysis of organic compounds.

Carbon and hydrogen are estimated by combustion, that is, by burning a known weight of the organic substance and determining separately the weights of carbon dioxide and of water produced. There is no simple method for directly estimating the proportion of oxygen present in an organic compound, but this is usually calculated by difference.

Two methods are described for the determination of nitrogen. Methods for estimating the halogens, sulphur, phosphorus, arsenic and antimony are also given.

Metals present in organic salts may be estimated by the ordinary methods of inorganic analysis.

ESTIMATION OF CARBON AND HYDROGEN BY COMBUSTION

376. In this method, a modification of that first described by Liebig, the organic substance is heated to redness with copper oxide, whereby its hydrogen is converted into water and its carbon into carbon dioxide. The water vapour is absorbed by granular calcium chloride or strong sulphuric acid and the carbon dioxide by concentrated potassium hydroxide solution. The process of combustion is assisted by a current of purified air or oxygen, which also serves to sweep out the products of combustion from the tube.

In general, the apparatus is set up as in Fig. 27.

That portion of the apparatus marked *A*, *B* and *C* is used for the purification of the air and oxygen, and is usually in duplicate, one set being used for air and one for oxygen. The air and oxygen are stored in the gas-holder *A*, and then passed through large U-tubes, *B* containing soda-lime, and *C* granular calcium chloride. The air or oxygen then passes through the sulphuric acid bubbler *D*, which primarily serves to indicate the rate of flow of the purified gas into the combustion tube *F*.

The apparatus for the purification of the entering gas, as well as that for the absorption of the products of combustion, is protected

from the radiant heat of the combustion furnace by squares of asbestos board or uralite *E,E*, which are slipped over the projecting ends of the combustion tube, close up to the sides of the furnace.

The water vapour produced is absorbed in the U-tube *G*, containing either granular calcium chloride or pumice stone soaked in strong sulphuric acid. The carbon dioxide is absorbed in a concentrated solution of caustic potash contained in the absorption bulbs *H*.

All connections between the various parts of the apparatus should be made with short lengths of stout rubber tubing, the glass

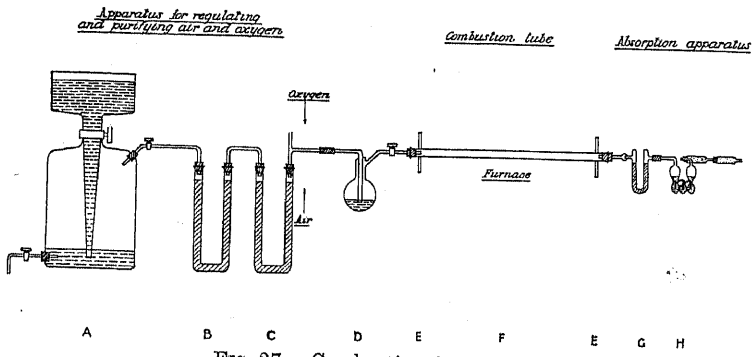


FIG. 27.—Combustion Apparatus.

ends being in contact whenever possible. Rubber bungs, not corks, should always be used.

Any of the many forms of gas-heated combustion furnaces may be used, but in general the most accurate results are obtained by the use of a furnace of considerable length.

377. The Combustion Tube.—The combustion tube, made of stout resistance glass, about 1·5 cm. in internal diameter, should project about 4 cm. from each end of the furnace. The sharp ends of the tube should be rounded off in the blowpipe flame and when cold the interior of the tube should be thoroughly washed, using a plug of wool or soft flannel material attached to a long piece of string. The tube should then be rinsed with distilled water and dried by a current of hot air.

THE FILLING OF THE COMBUSTION TUBE

378. The combustion tube (Fig. 27A) must be so fitted up that the products of combustion of the organic substance are made to pass over a long layer of coarse copper oxide (**379**) heated to

redness (*D*). The weighed amount of the substance, contained in a porcelain or silica boat (*B*), is placed immediately before this layer of copper oxide. Between the porcelain boat and the inlet of the combustion tube is placed an oxidised copper spiral (**380**), about 10 cm. in length (*A*), which serves to prevent the backward diffusion of any unburnt material. The coarse copper oxide is retained in position by short plugs of oxidised copper gauze or of asbestos (*C*, *C*).

If the compound contains nitrogen a spiral of reduced copper (**381**) is placed at the further end of the tube (*E*) in order to reduce any oxides of nitrogen present, which would otherwise be retained in the absorption tubes (see Fig. 27A, *B*).

If the compound contains halogen a spiral of metallic silver (*F*),

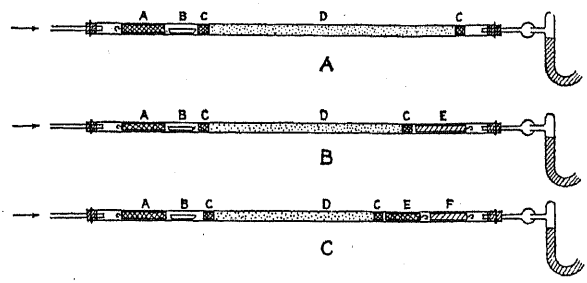


FIG. 27A.—Combustion Tubes.

A = Oxidised copper spiral.
B = Combustion boat.
C = Plugs of oxidised copper spiral or asbestos.
D = Coarse copper oxide.
E = Reduced copper spiral.
F = Silver spiral.

to decompose the volatile copper halides, must also be placed at the far end of the absorption tube (see Fig. 27A, *C*).

If the compound contains sulphur or phosphorus part of the coarse copper oxide should be replaced by a cylinder of copper gauze filled with small pieces of fused lead chromate, as the lead sulphate subsequently formed is much more stable than copper sulphate.

379. The Copper Oxide.—The copper oxide used for combustions must have been prepared by the direct oxidation of metallic copper, and is usually made by roasting short lengths of copper wire in a current of air. If the oxide has been made by precipitation or by the ignition of the nitrate it is unsuitable for use in organic combustions. Before use it is always advisable to heat the copper oxide to a dull red heat in a copper or nickel crucible in order to remove moisture and to destroy organic matter.

380. The Oxidised Copper Spiral.—The oxidised spiral is made by tightly coiling copper gauze about a stout copper wire to such a

thickness that it fairly easily fits the tube. The central copper wire is bent into a loop at one end so that the coil may be removed easily when required. It is repeatedly heated in the blowpipe flame and cooled in the air until thoroughly oxidised.

381. The Reduced Copper Spiral.—A spiral of copper gauze is made as described above and freed from grease by washing with a little ether. It is then superficially oxidised by heating in a large blowpipe flame and plunged whilst still hot into a stout tube containing 2 c.c. of methyl alcohol. The evolved vapours are allowed to burn at the mouth of the tube, which is then loosely corked and allowed to cool. When cold the spiral is freed from methyl alcohol by warming in a steam oven, and is then placed in a desiccator until required.

THE ABSORPTION APPARATUS

382. The apparatus for the absorption of the water vapour and carbon dioxide produced by the combustion is arranged as shown in Fig. 28.

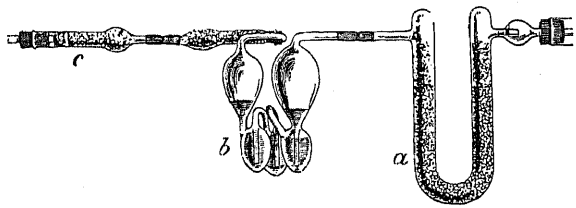


FIG. 28.—Absorption Tubes for Water and Carbon Dioxide.

The water vapour is absorbed in the U-tube *a*, which contains either granular calcium chloride (**383**) or pumice stone impregnated with strong sulphuric acid (**384**). This U-tube is so arranged that the bulk of the moisture condenses in the small bulb of the side tube, and can be removed with filter paper at the end of the experiment. The limbs of the U-tube are sealed off in the blowpipe flame when the apparatus has been filled.

The carbon dioxide is absorbed in the potash bulbs *b*, which is protected from the atmosphere by a second guard tube *c* (**385**).

383. Calcium Chloride Tube.—The U-tube should be filled with granular calcium chloride that has been sieved to remove dust and small particles. The limbs of the tube are then sealed off and a slow current of dry carbon dioxide passed through the tube for about an hour. This is a necessary procedure, as ordinary anhydrous calcium chloride contains basic compounds that absorb

carbon dioxide. The excess of carbon dioxide is then swept out of the apparatus by a current of dry air. So prepared the calcium chloride tube can be used for many combustions without refilling. *When not in use all absorption vessels should be closed with short lengths of stout rubber tubing plugged with small pieces of glass rod.*

384. Sulphuric Acid Absorption Tube.—Small pieces of washed pumice stone are covered overnight with strong sulphuric acid, and next day warmed on the water bath to decompose carbonates and chlorides present. The pumice stone is then washed with distilled water and dried in a porcelain dish over a naked flame. The dried pumice stone is placed in the U-tube and then soaked in pure sulphuric acid for about two hours. The excess of acid is allowed to drain away, the side tubes cleaned, and the main limbs of the U-tube sealed off in the blowpipe flame. So prepared the absorption tube can be used for many estimations without refilling.

385. The Potash Bulbs.—The carbon dioxide evolved in the combustion may be conveniently absorbed in a concentrated solution of potash, contained in a Geissler potash bulb tube. The Geissler bulb tube is almost invariably used (Fig. 29), although other forms of absorption bulb are obtainable. Great care must be exercised in the manipulation of the absorption bulbs, as they are exceedingly fragile.

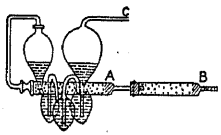


FIG. 29.—Potash Bulbs.

The bulb is filled three parts full with a solution of 60 gm. of caustic potash in 100 c.c. of water. This is effected most conveniently by dipping the inlet tube *C* into the solution of potassium hydroxide, and then applying a gentle suction to the exit tube. A guard tube *A*, containing granular calcium chloride, is attached to the exit tube and must be weighed with the absorption bulbs. This tube serves to prevent moisture being carried away from the potash bulb during the process of combustion. A second guard tube *B* protects the apparatus from atmospheric impurities. This guard tube is *not* weighed.

NOTE.—The caustic potash cannot be replaced by caustic soda in the absorption bulbs, as sodium carbonate is relatively insoluble in the alkali solution.

PROCESS OF COMBUSTION

386. Proceed to heat to redness the combustion tube containing the copper oxide and oxidised copper spirals in a current of purified air for at least half an hour, in order to remove all combustible matter and moisture. Allow the tube to cool, and place a soda-lime

tube in the end of the apparatus. Now weigh out about 0·20 gm. of the dry organic substance in the combustion boat and place the boat in the combustion tube, at the same time introducing the reduced metal spirals (**381**), if these are required. Attach the weighed absorption apparatus and ascertain that the whole is airtight.

Now heat the copper oxide and the metal spirals, at first gently and then to a dull red heat, gradually working towards the combustion boat, and at the same time strongly heating the oxidised copper spiral that precedes the boat. Start a slow current of air through the tube so that about two bubbles per second pass through the potash bulbs. Next heat the combustible substance very gently, at first by merely placing hot tiles above that portion of the tube, and finally by lighting the burners beneath. *It is absolutely essential that this operation should be carried out at a slow and even rate.* Continue the heating until the whole of the organic substance has been burnt away and until the copper oxide which was reduced in the early stages of the combustion has become reoxidised.

If a current of oxygen is used to facilitate complete combustion, it must finally be replaced by a current of air in order to displace the oxygen from the absorption tubes before weighing.

Should any moisture condense in the projecting end of the combustion tube it may be removed by gently warming with a hot tile held near.

When the combustion is completed the absorption units are detached and plugged and allowed to stand near the balance for half an hour before weighing. The combustion tube is allowed to cool in the furnace, the hot tiles of the furnace being left in position.

387. Calculation of Results.—If w gm. of the substance yields a gm. of water and b gm. of carbon dioxide, then the percentage of hydrogen in the compound is $\frac{100\,a}{9\,w}$ and the percentage of carbon is $\frac{300\,b}{11\,w}$.

388. Combustion of Organic Liquids.—Organic liquids that are not very volatile should be weighed in a small glass bulb with a capillary tube opening. This tube is placed in the combustion tube and the process of combustion carried out in the usual manner, special care being taken to guard against backward diffusion.

389. Combustion of very Volatile Liquids.—The liquid should be weighed in a special tube, conveniently made from a piece of ordinary glass tubing, as shown in

Fig. 30. The tube is first weighed alone, and then weighed again after the liquid has been introduced and both ends have been sealed. It is then placed either in a dish of cold water or in ice and salt, according to the degree of volatility of the liquid.

When the combustion tube has been heated to redness the horizontal end (*a*) of

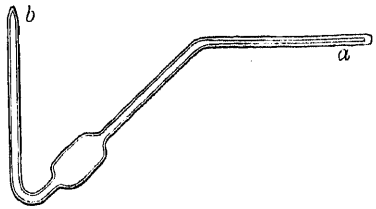


FIG. 30.—Weighing Tube for Volatile Liquid.

the bent tube is opened, and is at once pushed through a hole in the cork of the combustion tube, into which it must fit tightly.

The liquid is then allowed to rise in temperature and evolve its vapour, which will pass into the combustion tube and be burnt. As soon as the liquid has volatilised, the upright end (*b*) of the tube is snapped off, and air or oxygen is passed through the tube.

390. Gaseous Organic Substances are burnt by passing a known volume through the combustion apparatus.

ESTIMATION OF NITROGEN IN AN ORGANIC COMPOUND

391. General Remarks.—Two methods are described for the estimation of nitrogen. The **Dumas,** or **Absolute Method (392),** provides for the measurement of the gaseous nitrogen which is evolved when the substance is burnt with copper oxide. This process of analysis is applicable to all nitrogen-containing compounds, and may be regarded as the standard method.

In the **Kjeldahl Method (401)** the substance is heated with strong sulphuric acid and the nitrogen converted into ammonium sulphate, which is then estimated volumetrically. This process is used particularly for the estimation of nitrogen in liquid or moist bodies, and is especially useful for vegetable and animal products.

ESTIMATION OF NITROGEN BY COMBUSTION. DUMAS' METHOD

392. The organic substance is heated with copper oxide in an atmosphere of carbon dioxide gas. The constituent elements, nitrogen, carbon and hydrogen, are then evolved as nitrogen,

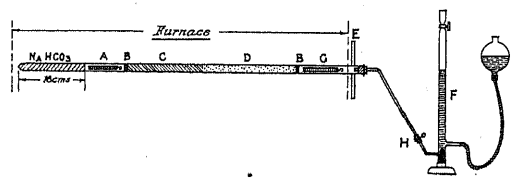


FIG. 31A.

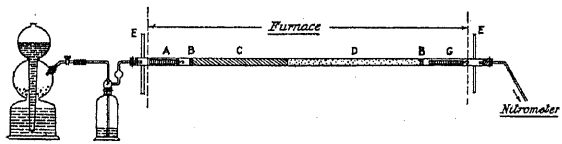


FIG. 31B.
Combustion Apparatus for Nitrogen.

carbon dioxide and steam respectively. These products are passed through cold strong potassium hydroxide solution into the measur-

ing vessel, where the nitrogen alone collects in the gaseous condition. The volume of gas thus obtained is corrected for temperature and pressure, and its weight is then calculated.

The current of carbon dioxide, used to sweep out all the air and the products of combustion from the tube, is produced either by heating pure sodium bicarbonate placed at one end of the combustion tube (Fig. 31A), or else it is passed into the tube from a separate carbon dioxide generator (Fig. 31B).

393. The Combustion Tube.—The tube should be about 1·4 cm. in diameter and of such a length that it will project about 3 cm. beyond the furnace. If arranged as in Fig. 31A, one end must be sealed off and the other end rounded at the edge to receive the rubber cork. With the tube arranged as in Fig. 31B, each end must project from the furnace and the edges must be rounded.

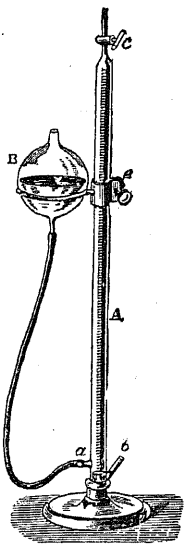


FIG. 32.—Nitrometer.

394. Filling the Combustion Tube.—The combustion tube is filled as shown in Fig. 31A or 31B. An oxidised copper spiral, prepared as described in paragraph **380**, is placed at *A*. Small plugs of asbestos fibre *B,B*, previously heated in the blowpipe flame, serve to prevent the copper oxide from becoming displaced. A layer of fine copper oxide *C* (**379**) is then introduced, and immediately followed by the substance to be analysed intimately mixed with about 20 gm. of fine copper oxide, as described below (**395**). A further small quantity of fine copper oxide is then introduced and the tube almost filled with coarse copper oxide *D*, so that there is just sufficient room left for the spiral of reduced copper *G* (**396**) within the furnace area. Pieces of asbestos board or uralite *E,E* protect the nitrometer (**397**), from the heat of the furnace. When the tube has been filled it should be inclined at a slight angle and gently tapped on the bench so as to ensure that the copper oxide is not so tightly packed as to prevent the gases passing through.

395. The substance to be analysed is finely powdered and sufficient weighed out to yield 20 or 30 c.c. of nitrogen. It is then mixed intimately in an agate pestle and mortar with about 20 gm. of fine copper oxide. The mixture is poured into the tube

through a dry copper funnel and rinsed in with some more copper oxide.

396. The Reduced Copper Spiral should be at least 10 cm. in length, and must be prepared from copper gauze, as described in paragraph **381**. It is for the purpose of reducing any oxides of nitrogen to nitrogen, before collection in the nitrometer.

397. The Nitrometer, shown in Fig. 32, consists of a graduated burette *A*, supported in a heavy base, and furnished with an accurately fitting stopcock *C* lubricated with vaseline. The burette is connected by a side tube *a* with the reservoir *B* by means of stout rubber tubing. A second side tube *b* is connected with the burette at a point below *a*, and is inclined upwards.

Mercury is poured in until it rises about 1 cm. above the joint *b*, and thus prevents the alkali solution entering the combustion apparatus. When not in use the tube *b* is closed with stout rubber tubing and a screw clip. The nitrometer is filled with a cold solution of 2 parts of potassium hydroxide dissolved in 3 to 4 parts of water, with the addition of a trace of powdered barium hydroxide to prevent frothing when in use.

The nitrometer is shown diagrammatically in Fig. 31A.

PROCESS OF COMBUSTION

398. The apparatus having been connected together as in Fig. 31A by means of stout rubber tubing, the burners under a part of the sodium bicarbonate are lighted, and the carbon dioxide evolved serves to expel the air from the tube. During this time the potash solution is emptied as completely as possible into the reservoir of the nitrometer. The stream of carbon dioxide is diminished and the coarse copper oxide and the reduced spiral heated to redness, care being exercised that the portion of the tube containing the substance is not heated by conduction.

The nitrometer is now filled by raising the reservoir and the issuing gas tested for freedom from air by allowing the carbon dioxide to be absorbed in the alkali solution. When no appreciable volume of air is collected above the potassium hydroxide solution during a period of several minutes the combustion of the organic compound may be commenced.

The burners beneath the oxidised copper spiral are lighted, and when this is at a dull red heat, heating is extended very slowly over the area occupied by the fine copper oxide and the compound. *The heating is so regulated that not more than two bubbles of gas are ascending the nitrometer at the same time.* Ultimately, when

all the tube is at a uniform red heat and the actual combustion completed, the residual sodium bicarbonate is heated and the nitrogen displaced from the tube by the carbon dioxide so evolved.

The nitrometer is now disconnected, the screw clip *H* on the rubber tubing closed, and the vessel stood in a cool place for some time.

The combustion tube is allowed to cool in the furnace, the furnace tiles being kept closed.

If the apparatus has been set up employing a separate carbon dioxide generator, precisely the same procedure is followed during the combustion, but special precautions have to be taken in the preparation of the gas, as described below (**399**).

399. The Carbon Dioxide Generator must be filled with small pieces of marble that have been boiled for some hours with water, in order to displace occluded air, and then allowed to cool under the water. The hydrochloric acid used must also be diluted with an equal volume of water and boiled for five minutes. The generator must not be attached to the combustion tube until all the air has been displaced from it. The issuing gas is bubbled through a wash bottle containing water, in order that the rate of flow may be readily observed, and to free it from traces of hydrochloric acid.

400. The Measurement of the Nitrogen.—The nitrometer having been allowed to cool, the levels in the burette and in the reservoir are adjusted in the normal manner and the volume noted. The temperature of the alkali solution is also recorded, as well as the barometric pressure. Tables are given on pages 326, 327, recording the weight of 1 c.c. of moist nitrogen under various conditions of temperature and pressure, and allowance has been made in these tables for the vapour pressure of strong caustic potash solution. Hence if w is the weight in milligrams of 1 c.c. of nitrogen under the conditions observed, and if v c.c. were obtained from W gm. of the substance, then the percentage, N, of nitrogen in the compound is given by the formula

$$\mathrm{N} = \frac{v \,.\, w}{10\,\mathrm{W}}.$$

ESTIMATION OF NITROGEN BY KJELDAHL'S PROCESS

401. This process is suitable for dry or moist solids and for liquid bodies, but is not applicable to compounds in which the nitrogen is directly combined with oxygen or nitrogen, as in the azo-, diazo-,

nitro-, nitroso- and azoxy-compounds and the esters of nitrous and nitric acids.

The substance is first heated with strong sulphuric acid, *free from nitrogen compounds*. The nitrogen of the organic body is thus converted into ammonium sulphate.

The acid solution is then heated with excess of sodium hydrate ; and the ammonia thus evolved is absorbed in a known volume of standard acid and determined volumetrically.

Strong Sulphuric Acid, free from ammonium sulphate and from oxides of nitrogen, is required for the process. The freedom of the acid from these substances can be ascertained by making a blank experiment.

402. Digestion with strong Sulphuric Acid.—A weighed quantity of the substance, 0·5 to 3·0 gm., is placed in a Kjeldahl flask made of resistance glass. The quantity taken depends on the amount of nitrogen in the compound. Twenty cubic centimetres of pure sulphuric acid and a very small quantity of copper sulphate or mercuric sulphate are then added, and the flask loosely stoppered with a small funnel as in Fig. 33 (*a*). The flask is then clamped in an inclined position and gently heated over a wire gauze in the fume chamber for about twenty minutes ; it is then allowed to cool somewhat, and about 8 gm. of dry powdered potassium sulphate are added. The addition of the potassium sulphate renders it possible to raise the temperature to which the liquid may be heated without boiling. The contents of the flask are heated almost to boiling until they become clear and practically colourless. The whole is allowed to cool and poured into 100 c.c. of distilled water, the flask also being washed out with a few cubic centimetres of water.

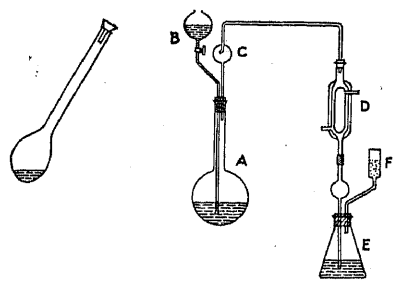


FIG. 33.—Kjeldahl Apparatus.

403. Distillation of the Ammonia.—The acid solution is placed in the flask *A*, of capacity about 500 c.c., as shown in the distillation apparatus, Fig. 33 (*b*).

In the tap funnel *B* is placed a solution of 40 gm. of sodium hydroxide dissolved in about 100 c.c. of water. This quantity of alkali is more than sufficient to neutralise all the sulphuric acid. The ammonia evolved passes through the alkali trap *C*, through

the condenser *D*, and is finally absorbed in a known volume of standard acid, say, 100 c.c. of N sulphuric acid, contained in *E*. The tube *F* contains glass beads, moistened with water, and serves to retain any traces of ammonia not absorbed in *E*.

The alkaline solution is run into *A*, and the whole distilled until all the ammonia has been absorbed in *E*. The condenser and the beads in *F* are washed through with a little distilled water, the washings added to the acid in *E*, and the whole made up to 200 c.c. The excess of acid is then estimated by titration with N/2 sodium hydroxide solution, using methyl orange as an indicator, and the amount of acid that has been neutralised by the ammonia obtained by difference.

ESTIMATION OF HALOGENS IN ORGANIC COMPOUNDS

404. General Remarks.—Four methods are described for the estimation of halogen in organic compounds. Each involves the complete decomposition of the substance and the estimation of the halogen as silver halide, either gravimetrically or volumetrically.

The method of *Piria and Schiff* (**405**) is applicable to all halogen compounds that are not appreciably volatile. The substance is fused with sodium carbonate and lime, and the resultant halide estimated gravimetrically.

The method of *Carius* (**406**) involves the decomposition of the substance with fuming nitric acid in the presence of silver nitrate in a sealed tube. It is unsatisfactory for the estimation of iodine compounds.

The method of *Stepanow* (**407**) is applicable to all aliphatic compounds and to those aromatic compounds that react when refluxed with alcoholic solutions of sodium alcoholates or are reduced by the action of sodium in alcohol. The halide produced is then estimated volumetrically. The method is fairly quick and accurate.

The method of *Liebig* (**408**) is the oldest method for this estimation, and is applicable to the largest number of compounds, but is somewhat tedious owing to the necessity of using large amounts of reagents. The substance is fused with a large excess of pure lime and the calcium halide estimated gravimetrically.

ESTIMATION OF HALOGEN BY THE METHOD OF PIRIA AND SCHIFF

405. This method is applicable to halogen compounds that are not readily volatile. About 0·2 gm. of the substance is intimately mixed with sufficient pure lime (4 parts) and anhydrous sodium carbonate (1 part) to just fill a fairly small nickel crucible (*a*) Fig. 34. This nickel crucible is then inverted in a larger nickel crucible (*b*), and the space between the crucibles filled with a mixture of the two alkalies. The smaller crucible should be completely covered with the mixture.

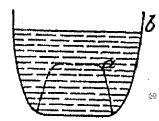


FIG. 34.—Halogen by Fusion.

The lid is placed on the larger crucible and the mixture heated over a small flame kept in constant motion, so that the sides rather

than the bottom of *b* are heated. The heating is gradually increased so that the organic compound is completely destroyed.

The mass is allowed to cool, extracted with water, and then with dilute nitric acid. After filtering, excess of silver nitrate is added and the silver halide estimated in the usual manner.

If the compound contains iodine, sodium carbonate alone is employed in the fusion. After extraction and acidification the solution is treated with a minimum of sulphurous acid to reduce any liberated iodine.

ESTIMATION OF HALOGEN BY THE METHOD OF CARIUS

406. The organic substance is mixed with fuming nitric acid and silver nitrate, and the mixture is then heated for several hours in a sealed glass tube. The halogen is thus obtained in combination with silver, and is weighed in this form.

The Process of Estimation.—Cut off a piece of thick-walled Jena glass tube or bomb tube, about 50 cm. in length and 1·5 cm. in diameter. Seal up one end in the blowpipe flame, being careful to make the end strong and round in shape, and to anneal the glass well by allowing it to cool down slowly, finally in the luminous flame. This is the digestion tube.

Weigh out accurately about 0·2 gm. of the substance in a small weighed piece of quill tubing which is not less than 4 cm. in length and is sealed at one end.

If the substance is a volatile liquid, it is sealed up in a small thin tube, or in a thin bulb tube. The bulb tube may be made from a thin-walled ignition tube, 0·5 cm. broad, by heating its closed end in the flame and blowing it out into a bulb about 1·5 cm. in diameter. When the tube is cold it is weighed, and the substance is introduced. The upper part of the tube is then drawn off and sealed by holding it in a blowpipe flame, and the two parts of the tube with the enclosed substance are weighed. The gain in weight of the tube gives the amount of substance taken. The portion of the glass drawn off from the bulb is weighed at once, and the weight is noted down for subsequent use.

Now introduce into the digestion tube about twice as much solid silver nitrate as is theoretically required to furnish sufficient silver to combine with the halogen. Then pour in 2 c.c. of fuming nitric acid, and push the tube containing the substance down the interior of the digestion tube until it reaches within about 5 cm. of the acid. The small tube will adhere to the glass surface, owing to its being wet with nitric acid. The greatest care must be taken not to allow the acid or its vapour to reach the substance in the open tube; if the substance is contained in a sealed tube or bulb this danger is avoided.

Now draw out and seal the open end of the digestion tube. For this purpose hold the tube in a slanting position, so that its contents remain undisturbed in their relative positions, and the acid does not reach the substance. Gradually heat the tube at about 10 cm. from its open end, rotating it continually in the flame, until its sides soften and thicken and begin to fall together. Then gradually draw off the upper part, leaving a thick-walled sealed capillary end, and carefully anneal this by cooling it first in the luminous flame and finally in the air.

Now place the tube in a loosely fitting wrought-iron tube, and

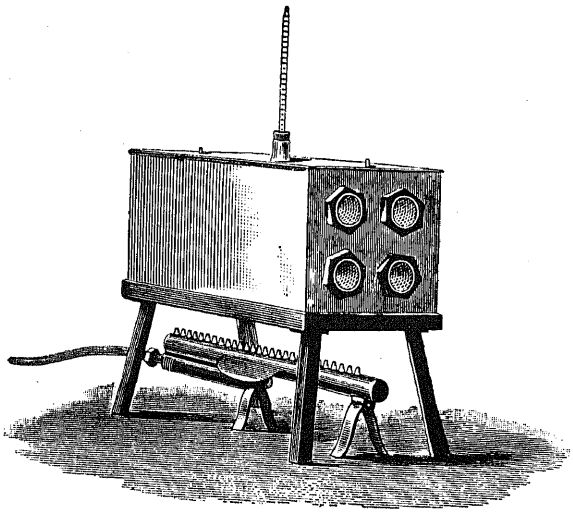


FIG. 35.—Air Bath for Heating Sealed Tubes.

close this with a screw cap in order to prevent accident if the glass should burst under the pressure to which it is subjected. It is well to wrap the tube in a sheet of asbestos paper before placing it in the iron tube, so as to lessen the risk of fracture. Then tilt the tube sufficiently to cause the acid to rinse the small tube down to the bottom, or if the substance has been sealed in a bulb tube break the bulb by shaking the digestion tube. The tube is now ready to be heated in the air bath (Fig. 35).

When the sealed tube has been inclosed in the wrought-iron tube of the air bath and the cap has been screwed on, introduce it into the broader tube of the air bath and light the burner. Watch the thermometer carefully, and allow the temperature to rise until it

reaches the desired temperature; then maintain the bath at this temperature for several hours by properly regulating the supply of gas to the burner.

A temperature of 300° C. is sufficient to ensure decomposition in all ordinary cases. A lower temperature will frequently suffice, and some simple bodies will be decomposed at a temperature of 150° C.

Then allow the bath and tube to become quite cold, take off the cover, and proceed to remove and open the tube in the following manner:

The tube inclosed in its protecting wrought-iron jacket is taken out of the air bath in the jacket, the cap is removed, and the capillary end is slid out of the jacket. Care must be taken not to allow the open end of the iron tube to face the person, since there may be very considerable gaseous pressure within the tube, and an explosion which may occur should take place away from the person. The capillary end projecting from the air bath is drained from any adhering liquid, is then heated in a Bunsen flame until the glass softens and the gas forces an exit and escapes.

When the substance requires to be heated for a long time with the acid to a high temperature, it is best to allow the tube to cool and to permit the gases to escape from the cold tube once or twice during the process of heating, the tube being sealed again each time before the heating is proceeded with. This precaution will often save the tube from bursting.

If there is any doubt about the oxidation of the substance being complete after the capillary has been opened in an ordinary determination, the tube should be sealed up and reheated.

As soon as the issue of gas ceases, the end of the digestion tube is cut off with a file, and the contents are rinsed out with water into a beaker. Any large pieces of the small glass tube or bulb are removed and washed, then dried in the steam oven and weighed, the weight of the end which was drawn off during the sealing, if a glass bulb was used, being added. The difference between this weight and that of the original bulb or tube represents the weight of the small pieces of glass which remain in the silver halide.

The acid liquid is then diluted and boiled for a few minutes, and the silver salt is filtered off (*Note*), washed, dried, and weighed. The weight of any small glass fragments, which has been already determined, is then deducted, and the true weight of the silver salt is thus obtained. From this the weight of the halogen and its percentage is calculated.

NOTE.—If iodine is present in the organic substance, the silver nitrate and silver iodide sometimes fuse together into a yellow mass. The silver nitrate must be removed from this mass, by heating it in the diluted liquid for one or two hours.

STEPANOW'S METHOD FOR ESTIMATING THE HALOGENS

407. Weigh out 0·2 to 0·3 gm. of the substance and place it in the flask of a reflux apparatus. Add 20–40 c.c. of 98 per cent. alcohol and heat on a water bath. Drop pellets of sodium down the condenser so as to produce a continuous vigorous action. The amount of sodium should be about twenty-five times that required by the reaction. The time taken for the additions should be at least thirty minutes, and the mixture should then be boiled for an hour.

Allow to cool somewhat, dilute the mixture with 20–40 c.c. of water and distil off the alcohol.

The sodium halide left is rendered strongly acid with dilute nitric acid, and estimated volumetrically by the thiocyanate (Volhard's) method.

This method is particularly useful when dealing with compounds containing easily replaceable halogen atoms, but is not satisfactory with aromatic substances with the halogen substituted in the nucleus, unless other electronegative groups, such as the nitro-group, are in the ortho- or para-position to the halogen atom. The method, when applicable, is of great value, because it is relatively simple and rapid. Good results are obtained with such substances as the halogen substituted aliphatic compounds, with benzyl chloride, with 2·4-chlordinitrobenzene, but not with chlorbenzene.

ESTIMATION OF HALOGEN BY THE METHOD OF LIEBIG

408. The powdered solid substance is mixed with lime or soda-lime, and the mixture is heated strongly; the halogen is thus obtained in combination with calcium.

The cooled mass is then dissolved in nitric acid, excess of silver nitrate solution is added to this liquid, and the halogen is precipitated and weighed in combination with silver.

The process is rendered somewhat tedious by the necessity of using a large quantity of nitric acid to neutralise and dissolve the alkaline mass. The operations of filtration and washing the precipitate and filter become, therefore, somewhat lengthy.

The Lime or Soda-lime which is used for the combustion should be free from chloride.

The quicklime may be readily prepared by breaking marble into small pieces of similar size, introducing it into a clay crucible, and heating it strongly in a muffle furnace for several hours. The lime thus prepared is removed from the crucible as soon as it is cold, and is preserved in a well-stoppered bottle.

The soda-lime in a granular condition is heated strongly to expel moisture, and is stored in a stoppered bottle.

Cleanse a piece of combustion tube, about 50 cm. in length and about 1 cm. in

diameter, close one end by drawing it out in the blowpipe flame, and fuse the sharp edges of the open end in the flame.

Fill about 5 cm. of the tube with the powdered lime or soda-lime, and add the weighed substance.

Now introduce another 5 cm. of the powdered lime or soda-lime into the combustion tube, and mix the accurately weighed substance with this portion by pushing down into the tube a long bright piece of wire which is bent like a corkscrew at its end, and turning this wire round in the powder and substance. Almost fill the rest of the tube with granular lime or soda-lime, and then insert a loose plug of asbestos.

A volatile organic liquid would be dropped into the combustion tube in a small tube or bulb with a capillary opening (**388**) after the first 5 cm. of lime powder have been introduced, or it may be introduced in the form of vapour, as is directed in paragraph **389**.

Either leave the end of the combustion tube open, or draw it out into a narrow tube which is bent obliquely and has its end just immersed beneath the surface of some water contained in a small beaker during the process of combustion.

Now lay the tube in the trough of the combustion furnace, and heat the front portion containing the granular lime to redness. When the lime is red-hot, gradually extend the heat to the mixture.

As soon as the decomposition is complete, transfer the contents of the tube to a beaker, after cutting off the narrow end of the tube if it has been drawn off. Then rinse out the tube with dilute nitric acid into the beaker (*Note*), and add more nitric acid and stir until the lime is completely dissolved. Now filter off any particles of carbon and glass, add an excess of silver nitrate solution to the clear liquid, and filter off, dry, ignite and weigh the precipitate.

NOTE.—If iodine is to be estimated it is necessary, before precipitating with $AgNO_3$, that sodium sulphite should be added during the treatment of the contents of the tube with nitric acid, to convert any free iodine or iodate into iodide.

ESTIMATION OF SULPHUR IN ORGANIC COMPOUNDS

409. The estimation of sulphur is accomplished by the destructive oxidation of the compound with the formation of sulphuric acid and subsequent precipitation with barium chloride. In the *Carius'* process (**410**) the oxidation is effected with fuming nitric acid in the presence of bromine, whereas in the *sodium peroxide* method (**411**) the same result is attained by alkaline fusion in the presence of sodium peroxide.

410. Carius' Method.—The oxidation of the substance is effected by the use of fuming nitric acid, $\Delta = 1{\cdot}50$, in a bomb tube precisely similar to that described for the estimation of halogen in paragraph **406**. About 0·2 gm. of the substance is used and digested with 2 c.c. of fuming nitric acid and two or three crystals of potassium bromide. No silver nitrate is added.

After heating in the air bath, the bomb tube is cooled and opened, as previously described, and the contents washed into a porcelain dish with distilled water. The solution is evaporated

to small bulk and the sulphuric acid present estimated as barium sulphate by precipitation with a boiling solution of barium chloride.

411. Sodium Peroxide Fusion.—About 0·2 gm. of the substance is placed in a nickel crucible and intimately mixed with about 5 gm. of the fusion mixture, which contains 2 parts of anhydrous sodium carbonate to 1 part of sodium peroxide. The whole is then covered with a deep layer of the fusion mixture.

The crucible is first heated very gently over a small flame and the temperature gradually increased until the whole fuses to a clear liquid without further effervescence. The mass is allowed to cool and dissolved out with distilled water. The crucible is heated in the solution with the addition of a little bromine, added in order to oxidise any nickel sulphide present. The hot solution is filtered, excess of hydrochloric acid added, and the sulphur estimated as $BaSO_4$ by the addition of barium chloride solution.

It is apparent that this method cannot be applied to volatile compounds.

THE ESTIMATION OF ARSENIC IN ORGANIC COMPOUNDS

412. Weigh out from 0·2–0·3 gm. of the finely powdered substance and mix it, in a nickel crucible, with a mixture composed of 10 gm. of sodium peroxide and 20 gm. of anhydrous sodium carbonate, a portion of the latter being reserved for spreading over the mixture to prevent loss by spitting. Apply a *gentle* heat for about fifteen minutes, and complete the fusion by raising the temperature to dull redness for five minutes. Extract the contents of the crucible with water, filter if necessary, acidify with HCl, render alkaline with ammonia, and precipitate as magnesium ammonium arsenate in the usual manner, and weigh as pyroarsenate. Since the results are usually high, it is better to redissolve the precipitate and reprecipitate with ammonia before igniting to pyroarsenate.

THE ESTIMATION OF ANTIMONY IN ORGANIC COMPOUNDS

413. The antimony compound is fused with sodium carbonate and sodium peroxide, as in the case of arsenic (**412**). The melt is dissolved in distilled water, acidified with hydrochloric acid, sodium sulphite added, and boiled until the excess of sulphur dioxide is driven off. The antimony is estimated either by precipitation as sulphide or by titration with potassium bromate solution.

THE ESTIMATION OF PHOSPHORUS IN ORGANIC COMPOUNDS

414. Phosphorus in organic compounds is conveniently estimated by methods similar to those described for sulphur. Oxidation is usually effected by fuming nitric acid as in *Carius'* method.

The procedure adopted is precisely the same as that described under the estimation of halogen in paragraph **406**, page 284, except that no silver nitrate is added.

The solution obtained is neutralised with ammonia and the phosphoric acid present precipitated with magnesia mixture as magnesium ammonium phosphate, $MgNH_4PO_4$, and afterwards ignited and weighed as magnesium pyrophosphate.

THE ESTIMATION OF PHOSPHORUS IN ORGANIC COMPOUNDS

414. Phosphorus in organic compounds is conveniently estimated by methods similar to those described for sulphur. Oxidation is usually effected by fuming nitric acid as in *Carius'* method.

The procedure adopted is precisely the same as that described under the estimation of halogen in paragraph **406**, page 284, except that no silver nitrate is added.

The solution obtained is neutralised with ammonia and the phosphoric acid present precipitated with magnesia mixture as magnesium ammonium phosphate, $MgNH_4PO_4$, and afterwards ignited and weighed as magnesium pyrophosphate.

SECTION V

MOLECULAR WEIGHTS BY CHEMICAL AND PHYSICAL METHODS. ESTIMATION OF TYPICAL GROUPS AND ISOMERS

DETERMINATION OF MOLECULAR WEIGHTS

420. Chemical methods are usually applied to acidic or basic organic substances which are not volatile without decomposition. They depend upon the formation of definite salts, and require a knowledge of the basicity or acidity of the substance.

The physical methods depend upon the depression of the freezing-point or the elevation of the boiling-point of a solvent in which the substance has been dissolved. They are applicable to many organic and to some inorganic substances.

Other physical methods are subsequently described, which are applicable only to volatile substances and depend upon determining their vapour densities.

DETERMINATION OF THE MOLECULAR WEIGHT OF AN ORGANIC ACID

421. Precipitation Method.—The molecular weight of an organic acid may be determined by preparing an insoluble metallic salt from the acid, and then estimating the weight of the metal in a known weight of the pure salt.

Since silver is a monovalent metal and forms many insoluble salts, the silver salt is generally selected ; but in certain cases the barium or lead salt is converted into the sulphate by evaporation with strong sulphuric acid and subsequent ignition.

Thus the combustion of pure acetic acid gives the empirical formula CH_2O for this acid, and it is evident that either this formula or some multiple of it will represent the molecule of acetic acid.

Only one acetate of the monovalent metals can be obtained, and acetic acid is accordingly inferred to be monobasic.

The molecular weight of acetic acid may therefore be determined by preparing pure dry silver acetate, and then igniting a known

weight of this salt and weighing the residual silver. From this result the weight of the silver salt, which contains 107·98 parts of silver, may be found by calculation. This will be the molecular weight of the silver salt, and by subtracting from this molecular weight the atomic weight of silver, and adding that of hydrogen, the molecular weight of the acid will be obtained.

EXAMPLE.—Two grams of pure dry silver acetate gave on ignition 1·2934 gm. of silver.

Now the weight of silver thus found will stand in the same ratio to the atomic weight of silver, as the weight of the silver acetate, which was taken, does to the molecular weight of silver acetate.

Therefore the molecular weight of silver acetate $= \frac{107{\cdot}98 \times 2}{1{\cdot}2934}$ $= 166{\cdot}97$. And the molecular weight of the acid $= 166{\cdot}97 - 107{\cdot}98 + 1 = 59{\cdot}99$. This molecular weight corresponds to the molecular formula $C_2H_4O_2$.

From a polybasic acid more than one corresponding salt of a monovalent metal may usually be prepared. These salts will contain different percentages of the metal, and from a study of the relative proportions of metal present in them, the basicity of the acid may usually be inferred.

For Practice in the Determination prepare some pure silver succinate by adding a moderately strong solution of silver nitrate to a solution of sodium or ammonium succinate. Filter off the silver succinate, remove dissolved salts from it by washing, and dry the salt at as low a temperature as possible.

Weigh accurately about 1 gm. of the silver succinate into a covered porcelain crucible of known weight, heat it very gently at first, but finally to a red heat for a short time, and weigh it; then repeat the processes of heating and weighing until the weight of the residual silver is constant.

Calculate the molecular weight in the way already described. Since, however, succinic acid is known to be dibasic, it is evident that $2 \times 107{\cdot}98$ must be subtracted from the molecular weight of the silver succinate, and 2×1 must be added to the remainder, in order to obtain the molecular weight of the acid.

422. Titration Method.—By this method the equivalent of an acid may be determined by titration with standard alkali. If the basicity of the acid is known, the molecular weight can be calculated. Since most organic acids are "weak," a strong alkali, such as baryta or caustic alkali (free from carbonate), must be used for the titration, with phenol phthalein as indicator.

For Practice in the Determination weigh out 2·5 gm. of succinic acid and dissolve in 250 c.c. of water, and titrate 25 c.c. with N/10 baryta. From the result calculate the equivalent of succinic acid. Since succinic acid is a dibasic acid, this value will require multiplying by two to give the molecular weight.

Additional methods, that may be applied to the determination of the molecular weight of acids, are described in paragraphs 444 *et seq.*

DETERMINATION OF THE MOLECULAR WEIGHT OF AN ORGANIC BASE

423. Certain organic bases, notably the alkaloids, combine with hydrogen chloride and platinum chloride to form double salts, which resemble in constitution the double chloride of ammonium and platinum, $(NH_3)_2H_2PtCl_6$, the organic base taking the place of the NH_3.

The molecule of the double salt therefore usually contains two molecules of the organic base, and if B represents a monovalent organic base, the general formula of the double salt will be $B_2H_2PtCl_6$. When the molecular weight of this organic double salt is known, the value of B can be calculated, since the weight of the other elements present in the molecule is known and can therefore be subtracted.

The method of procedure is identical in principle with that which has been already described (**421**). The pure dry double salt is prepared, and a suitable quantity of it is weighed; this is then ignited in the air until it is free from carbon, and the weight of the residual platinum is ascertained.

The molecular weight of the double salt is then obtained from the following proportion statement:

$$\left\{\begin{matrix}\text{The weight of}\\ \text{Pt found}\end{matrix}\right\} : \left\{\begin{matrix}\text{atomic weight}\\ \text{of Pt}\end{matrix}\right\} :: \left\{\begin{matrix}\text{weight of double}\\ \text{salt used}\end{matrix}\right\} : \left\{\begin{matrix}\text{molecular weight}\\ \text{of double salt.}\end{matrix}\right\}$$

The molecular weight of a monovalent base is then found by subtracting from the molecular weight of the double salt the weight represented by H_2PtCl_6, and dividing the remainder by 2.

EXAMPLE.—2·32 gm. of caffeine platinichloride yielded 0·57 gm. of platinum. Hence the molecular weight of the double salt

$$= \frac{195{\cdot}5 \times 2{\cdot}32}{0{\cdot}57} = 795{\cdot}7.$$

Therefore the molecular weight of caffeine

$$= \frac{795{\cdot}7 - 410{\cdot}2}{2} = 192{\cdot}7.$$

For Practice in the Determination dissolve some pure caffeine or

para-toluidine in dilute hydrochloric acid, and add to the solution a moderate quantity of platinum chloride solution. Filter off the yellow or orange precipitate of the double salt, wash it about six times with alcohol, and dry it in the steam oven.

Now weigh out 1 gm. of this double salt into a weighed porcelain or platinum crucible, and heat it gently at first and then strongly. Continue the ignition until all the carbon is burnt away, stirring occasionally so as to promote the combustion of the carbon. Then weigh the residual platinum, and repeat the processes of heating and weighing until the weight of the platinum is constant. From this weight calculate the molecular weight of the base as described above.

DETERMINATION OF MOLECULAR WEIGHT BY THE FREEZING-POINT OR CRYSOSCOPIC METHOD (RAOULT)

424. The molecular weight of a substance may often be determined by the lowering of the freezing-point of a solvent in which the substance has been dissolved. This method is of special value in the case of substances whose molecular weights cannot be determined by the preceding methods, or by taking their vapour densities.

The method depends upon the fact that if quantities of different substances, which are proportional to their molecular weights, are dissolved in equal amounts of the same solvent, the freezing-point of the solvent is in every case depressed to the same extent. This depression varies directly with the amount of substance used, and inversely with the amount of the solvent.

Hence the depression of the freezing-point of the solvent, which is caused by dissolving the molecular weight in grams of a body of known molecular weight in a known weight of the solvent, is first ascertained. The molecular weight of any other substance can then be readily found, if a known weight of that substance is dissolved in a known weight of the same solvent, and the depression of the freezing-point which is thus caused is noted.

The Formula required for Calculating the Molecular Weight is deduced as follows :—

If M = the molecular weight of the substance dissolved ;
K = the *Molecular Coefficient of Depression*, or the depression of freezing-point produced by dissolving the molecular weight of the substance in grams in 100 gm. of the solvent ;
W = the weight in grams taken of the substance, the molecular weight of which is required ;
S = the weight of solvent ;
D = the observed depression of freezing-point ;

Then the depression (D) is proportional to the number of gram-molecules of substance which have been dissolved in 100 gm. of solvent, or to $\frac{W}{M} \times \frac{100}{S}$: hence

$$D : K :: \frac{W \times 100}{M \times S} : 1, \text{ or}$$

$$D = K \frac{W \times 100}{M \times S}, \text{ and } M = K \frac{W \times 100}{D \times S}$$

or $M = K\frac{P}{D}$, where P is the percentage of the substance dissolved and D is the depression of freezing-point.

425. The Process of Determination is conveniently carried out in the apparatus of Beckmann (Fig. 36).

The glass tube *A* contains a stirring rod made of stout platinum or nickel wire, and a thermometer *D* which can indicate hundredths of a degree.

The capillary tube of the thermometer usually has a bulb at the top, which can receive some of the mercury, and thus enable the height of the mercury thread to be adjusted to suit various freezing-points. The variation in the quantity of mercury present in the stem of the thermometer in different pairs of determinations does not affect the accuracy of the result, because only the difference between the freezing-points of the solvent and of the solution is required and not the actual temperatures of freezing.

A weighed quantity of the solvent is introduced into the tube *A*, which is then placed in a somewhat wider tube *B*, and an air jacket is thus formed between the tube *A* and the outer vessel *B*. The external vessel *C* contains a stirring rod and either water or a freezing mixture, the temperature of which must be from 2° to 5° below the freezing-point of the solvent.

The thermometer is observed while the liquid is constantly stirred. At first the mercury sinks below the true freezing-point, but it rises again as the freezing commences. The highest position of the mercury is read.

When the freezing-point of the solvent has been ascertained as the mean of several determinations, a known weight

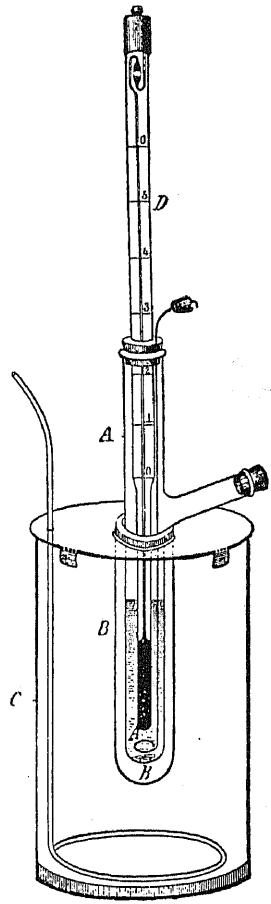


FIG. 36.—Beckmann's Freezing-point Apparatus

of the substance, the molecular weight of which is required, is introduced through the side tube into *A*. The liquid is then thoroughly stirred until the substance is dissolved, and the temperature of freezing is again noted. The "ice," which consists only of the solidified solvent, will now form at a lower temperature than before, and the difference between the two temperatures gives the lowering of the freezing-point (*D*).

The final accurate determination of the freezing-point must be effected in all cases by removing the tube from the jacket, and occasionally dipping it into the freezing mixture and moving it round until the liquid freezes. When this takes place the tube is immediately removed from the mixture, wiped dry, and placed in the air jacket once more. The "ice" will probably have melted by this time, if not allow it to do so, then attach the air jacket *B* and immerse it in the cooling mixture. Now stir constantly, carefully observing the freezing and noting down the highest temperature, as has been described above.

The molecular weight (M) is then calculated from the difference between the two freezing-points which have been noted, by means of the formula given on page 295.

A series of determinations may be obtained, if necessary, by adding successive quantities of the substance to the same quantity of solvent.

If the Molecular Coefficient of Depression (K) is unknown it can readily be ascertained by dissolving a definite quantity of a substance of known molecular weight in a weighed quantity of the solvent. The value of K is then calculated from the equation on page 295. The values of K for a few common solvents are for :

Water	18·7
Acetic acid	38·8
Benzene	49·0
Phenol	75·0

For Practice in the Method use dilute solutions of urea in water or of menthol in glacial acetic acid.

DETERMINATION OF MOLECULAR WEIGHT BY THE BOILING-POINT, OR EBULLIOSCOPIC METHOD

426. When a solid substance is dissolved in a definite quantity of a solvent, the boiling-point of the solvent is raised by an amount proportional to the number of gram-molecules of the dissolved substance.

A convenient and rapid process for the determination of mole-

cular weights of solids, by the elevation of the boiling-point of the liquid in which they are dissolved, is described below. It is a modification by Walker and Lumsden of the Landsberger method.

When the vapour from a boiling liquid is passed into another portion of the same liquid which contains a substance in solution the vapour is condensed in the solution, and the heat thus generated raises the temperature of the solution to its boiling-point.

This principle is applied in the process which is described below. The vapour from the boiling liquid is first passed through another portion of the liquid until the boiling-point is constant.

The temperature is then observed and a weighed quantity is added of the substance whose molecular weight is to be determined. The vapour of the solvent is then passed again until the substance is dissolved and the boiling-point of the solution is constant. The thermometer bulb must be immersed in the solution, as the vapour gives the boiling-point of the solvent, which is lower than that of the solution.

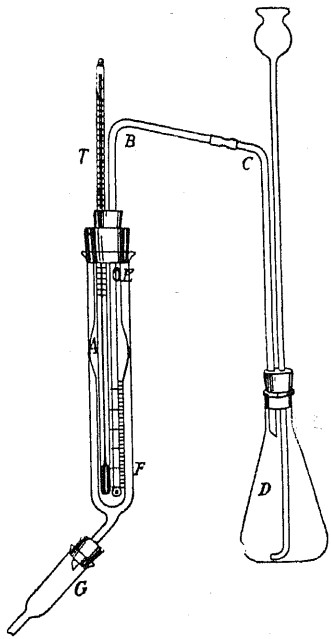


FIG. 37.—Molecular Weight by Elevation of Boiling-point.

Either the weight or the volume of the solution of the substance is now determined. In practice it is more convenient to measure the volume of the solution at its boiling-point and to deduce its weight from this volume, but a somewhat more accurate result is obtained by weighing the solution.

From the weight of the solution thus determined and the elevation of boiling-point of the solvent, the molecular weight of the substance can then be calculated. In the arrangement devised by Landsberger the escaping vapour is made to form a jacket round the boiling solution; by this means the errors arising from superheating and radiation are largely reduced.

The Apparatus required for the process is shown in Fig. 37.

It consists of a bulbed inner vessel *A*, which contains the

solution of the substance. This vessel is connected by a tube *B*, *C* with a flask *D* containing the solvent to be boiled. The vapour issuing from this flask passes through the solution in the vessel *A*, and escapes through a hole *E* into the jacket *F*, and thence into the condenser *G*. The capacity of the inner vessel *A* is indicated by cubic centimetre graduations, and the vessel contains a thermometer *T*, the stem of which is at least subdivided into tenths of a degree. In order to secure uniform and regular boiling of the liquid in the flask *D* a few pieces of unglazed tile are introduced, and a fresh piece of tile is added each time the boiling is started for a determination.

The Method.—Place from 5 to 10 c.c. of the solvent in the vessel *A* and about 150 c.c. of the solvent, together with a few pieces of unglazed tile, in the flask *D*. Connect the parts of the apparatus as is shown in the figure, and then boil the liquid in the flask. The vapour will pass into the vessel *A* and will quickly raise the temperature of the solvent to the boiling-point. When the temperature becomes constant, read the thermometer to the hundredth of a degree by means of a lens. This temperature is the boiling-point of the solvent.

Now disconnect the tubes *B*, *C* and pour out most of the condensed solvent from the vessel *A*, leaving about 10 c.c. Introduce from 0·5 to 1 gm. of the substance into the vessel, place a fresh piece of tile in the liquid in the flask *D*, connect the tubes *B*, *C* as before, and start boiling the liquid again. The thermometer will rise rapidly, and will remain approximately constant at a temperature a little higher than the boiling-point of the pure solvent. The boiling-point of the solution will then slowly but continuously decrease as the quantity of liquid in the vessel *A* increases by condensation of the vapour.

As soon as the highest temperature has been attained, read the thermometer accurately, stop the boiling in the flask, disconnect the tubes *B*, *C*, remove the cork with the tube and thermometer, and quickly read the volume of the solution. The boiling-point of the solution is thus determined, and the difference between this boiling-point and that of the solvent gives the rise of boiling-point which is due to the presence of the substance.

Further determinations should be made by using the solution already present in the vessel *A*. For this purpose a fresh piece of tile is placed in the flask *D* and the boiling is started again. After two or three minutes' boiling, readings of temperature and of volume are taken as before. These operations are repeated, and several determinations of the molecular weight can be obtained

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in this way with the same quantity of the substance in the course of half an hour.

When the molecular weight of the substance is high, or its solubility is small, greater accuracy is desirable. To secure this the solution of the substance in the vessel *A* is weighed, after the removal of the thermometer and tube, at the end of the first determination, and the experiment is repeated after an additional quantity of the substance has been introduced.

The Methods of Calculating the Molecular Weight from the volume and from the weight of the solution are shown below. If

w = the weight of substance dissolved;
V = the volume of the solution in cubic centimetres;
D = the elevation of boiling-point observed;
K′ = the elevation for 1 gram-molecule of substance dissolved in 1 c.c. of solvent;
M = the molecular weight of the dissolved substance;

Then since there are $\frac{w}{M}$ gram-molecules in V c.c. of solution, there will be $\frac{w}{MV}$ gram-molecules in 1 c.c. of solution.

If the elevation for 1 gram-molecule in 1 c.c. of solvent = K′, then the elevation for $\frac{w}{MV}$ gram-molecules $= \left(\frac{w}{MV}\right) \times K' = D$, whence

$$M = \frac{K'w}{VD} \quad (1).$$

If, on the other hand, the solution is weighed each time, the following formula is arrived at by a similar process of reasoning:

$$M = \frac{Kw}{WD} \quad (2),$$

where K = the elevation for 1 gram-molecule in 1 gm. of solvent, and W = the weight of the solvent.

NOTE.—If S = the specific gravity of the solvent at its boiling-point, then $V = \frac{W}{S}$ and $K' = \frac{K}{S}$.

The values of K′ and K for different solvents are as follows:

Solvent.	K′.	K.
Alcohol	1,560	1,150
Ether	3,030	2,110
Water. . . .	540	520
Acetone . . .	2,220	1,670
Chloroform . . .	2,600	3,660
Benzene . . .	3,280	2,670

For Practice in the Process, about 0·5 to 1 gm. of the substance, according to its solubility, should be used. The following substances and solvents will be found suitable: Urea in water; benzoic acid in absolute alcohol; naphthalene in chloroform; and camphor in acetone.

DETERMINATION OF MOLECULAR WEIGHTS BY VAPOUR DENSITY METHODS

427. Introductory Remarks.—By the term "vapour density" is usually meant the density or specific gravity of a vapour referred to that of hydrogen as unity.

Since the molecular weight of a substance is numerically equal to twice its vapour density with respect to hydrogen, the determination of the vapour density of a substance furnishes a means of ascertaining its molecular weight. This method is supplementary to others which have been already described.

Among the methods more usually employed are that of Victor Meyer (**428**), in which the volume occupied by the vapour of a known weight of the substance is measured, and of Dumas (**432**), in which the weight of a known volume of vapour is determined. The latter method is somewhat more complicated and requires a larger amount of the substance.

THE MEYER VAPOUR DENSITY METHOD

428. This method determines the volume of the vapour which is produced from a known weight of a volatile substance, by measuring the volume of air which the vapour displaces.

The volume of the displaced air is measured in cubic centimetres at atmospheric temperature and pressure, and while saturated with aqueous vapour; and from this the corrected volume of the air when dry and under normal conditions is calculated. This will represent the volume which the vapour of the substance would possess if it could exist under normal conditions. The weight of an equal volume of hydrogen is then found by multiplying the above number of cubic centimetres by 0·00009, and the density of the vapour of the substance is obtained by dividing the weight of the substance by this weight of hydrogen.

429. The Apparatus which is employed for the determination is shown in Fig. 38.

The inner vapour tube *b* is long and narrow, and is enlarged into a cylindrical bulb below. The whole tube has a capacity of about 200 c.c., and is somewhat broader at the top so as to admit of being closed by the insertion of a tightly fitting rubber cork. A

short distance below the top a bent capillary delivery tube *c* enters at right angles.

A broad outer tube *a*, which is enlarged into a bulb at the bottom, serves as a heating jacket for the inner vapour tube. A liquid, which has a much higher boiling-point than that of the liquid whose vapour density is to be determined, is placed in the bulb of this jacket.

Water is frequently used in the outer jacket; but bodies of higher boiling-point than water, such as amyl alcohol (B.P. 131°), aniline (B.P. 184°), and sulphur (B.P. 444°), are sometimes required. A suitable form of air jacket around the inner tube may replace the vapour; and the inner tube may be made of porcelain and be immersed in melted lead, or in the vapour of boiling zinc, when a higher temperature is required.

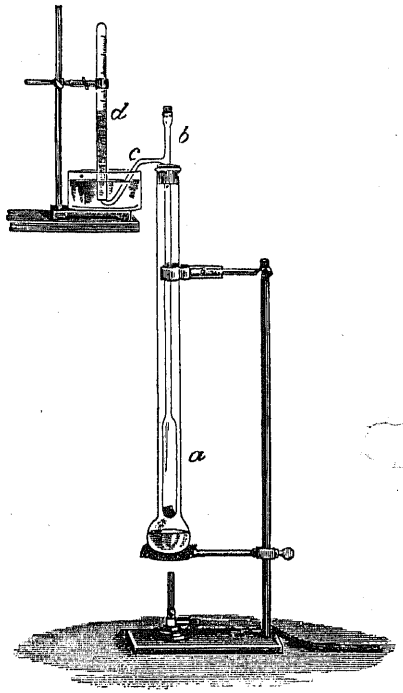


FIG. 38.—Meyer's Vapour Density Apparatus.

A measuring tube *d*, about 100 c.c. in capacity and graduated into fifths of a cubic centimetre, is filled with water and is inverted in a vessel of water. This stands at a convenient height for collecting the air escaping through *c*. A laboratory stool, placed upon the working bench, is generally of suitable height for supporting the vessel of water.

430. The Process of Estimation.—For practice in the method, the vapour density of pure ether may be determined in the following manner:—

The ether used for the estimation must have been purified as follows: It is first freed from alcohol by washing it with salt water, and then dried by being shaken with powdered calcium chloride. The last traces of water are now removed by dropping into the ether some clean slices of sodium, and allowing the liquid to stand for several hours in a loosely corked flask until no more bubbles of hydrogen escape from the surface of the sodium. The ether is then distilled off through a dry condenser into a clean dry bottle, the first portion of the distillate being rejected and only that portion being collected which boils at 34·5° C.

The apparatus is fitted up as is shown in Fig. 38. The interior of the inner tube having been thoroughly cleaned and dried, the bottom is padded inside with dry asbestos, sand or mercury, and the top is closed by a rubber cork. The bulb of the jacket tube is then half-filled with water, and the vapour tube is fitted centrally into the mouth of the outer tube by pressing in the two halves of a bisected cork, in which small openings are made for the escape of steam. The collecting trough is now arranged at such a height that the curved end of the delivery tube dips beneath the water when the tube is clamped in position over the burner. The water in the outer tube is then heated to boiling, and is kept boiling vigorously by the Bunsen burner, so as to cause steam to escape through the cork in the top of the jacket tube.

As soon as no more air bubbles escape from the delivery tube *c* through the water in the trough, the rubber cork is loosened in the top of the vapour tube, since the air within it has reached steam-

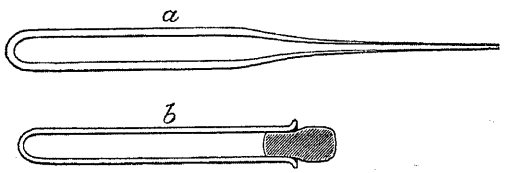


FIG. 38A.—Weighing Tubes.

is heat and the tube is therefore ready for the determination. The measuring tube *d* is filled with water and is clamped in position over the end of the delivery tube *c*.

Meanwhile a little glass tube about 3 cm. in length is made out of quill tubing, one end being closed and the other being drawn out to a capillary. The tube is shown drawn to actual size in Fig. 38A, *a*. The tube is weighed, and is then heated, and allowed to cool with its capillary point immersed in pure ether until a suitable quantity of the liquid ether has been introduced. The tube is then reweighed with the capillary end open. Its gain in weight gives the weight of the ether taken for the experiment.

The small glass tube may be conveniently replaced by a small weighing bottle fitted with a glass stopper (Fig. 38A, *b*).

The tube containing the ether is then at once dropped into the inner tube, which is immediately closed by the rubber cork. The ether will begin to boil, and its vapour will displace air from the inner tube, which will escape in a stream of bubbles into the

measuring tube. As soon as no more bubbles escape, the cork of the inner tube b is removed.

The measuring tube d is then removed to a tall cylinder of water, which should be at the temperature of the air. The tube is wholly immersed in the water, and as soon as its contents have gained the temperature of the water the tube is raised until the water inside and outside are at the same level. The volume of the air is then carefully read, and the temperature of the water and the barometric pressure are noted at the same time.

431. Calculation of Results.—All the data necessary for the calculation of the vapour density have now been obtained.

Let S = the weight of substance taken.
t = the temperature of the water in the cylinder.
v = the observed volume of the air in cubic centimetres.
p = the barometric pressure reduced to 0°.
w = the tension of water vapour at t°.
0·00009 = the weight of 1 c.c. of hydrogen.

$$\text{The vapour density} = \frac{\text{S} \times 760 \times (1 + 0{\cdot}003665t)}{v \times (p - w) \times 0{\cdot}00009}.$$

EXAMPLE.—In a determination of the vapour density of ether the following numbers were noted down :

Weight of ether taken	= 0·073 gm.
Temperature of water	= 21·5° C.
Volume of air displaced	= 25·3 c.c.
Barometric pressure at 0°	= 748·6 mm.
Tension of aqueous vapour	= 19·07 mm.

Hence the vapour density

$$= \frac{0{\cdot}073 \times 760 \times (1 \times 0{\cdot}003665 \times 21{\cdot}5)}{25{\cdot}3 \times (748{\cdot}6 - 19{\cdot}07) \times 0{\cdot}00009} = 36{\cdot}07.$$

THE DUMAS VAPOUR DENSITY METHOD

432. This method determines the weight of a definite volume of the vapour of the substance, which has been measured at a known temperature and pressure. From this result the volume which the vapour would possess, if it could exist under normal conditions of temperature and pressure, is calculated. The weight of an equal volume of hydrogen is then obtained by calculation, and the vapour density of the substance is found by dividing the weight of the vapour by that of the hydrogen.

433. The Apparatus required for the process is shown in Fig. 39. A large thin glass bulb, with its neck drawn out, is used for con-

taining the vapour : it has a capacity of about 200 c.c. Such a bulb may be purchased, or may be made by drawing out the neck of a round flask. After the liquid has been introduced, the bulb is supported in a double clamp, and is immersed in a suitable liquid contained in a large vessel. An enamelled iron water bath, placed on a tripod stand and heated by a gas burner, serves the purpose well. The temperature of the liquid in the bath is taken by means of a thermometer, the bulb of which is placed near the middle of the vapour bulb.

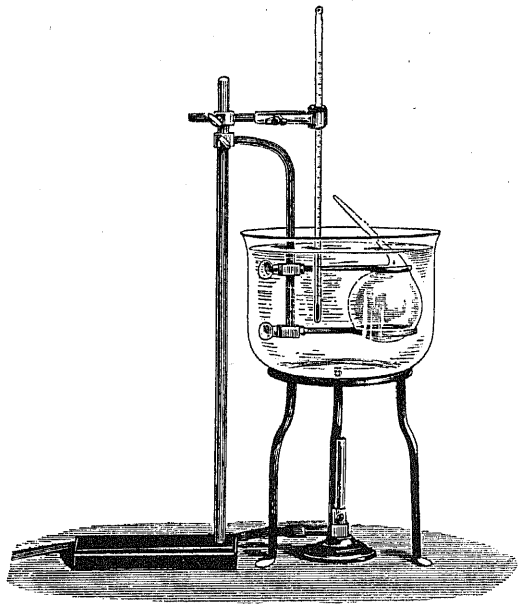


FIG. 39.—Dumas' Vapour Density Apparatus.

434. The Process of Estimation.—For practice in the process, the vapour density of pure benzene may be determined in the following manner :

The empty apparatus having been arranged as is shown in Fig. 39, the bulb is removed together with its clamp. The bath is then nearly filled with water, which is heated to boiling.

Meanwhile the clean dry bulb is weighed, after remaining in the balance case for some time. About 20 c.c. of the pure benzene are then introduced into the bulb by heating it and allowing it to cool with its open end immersed in the liquid.

The bulb is now fixed in its clamps and is immersed in the gently

boiling water in the bath, with the end of the tube projecting about 2 cm. above the surface of the water. The bulb is clamped in this position. The thermometer is also at once fixed, with its bulb level with the middle of the vapour bulb and close to it.

The benzene will boil vigorously, and the vapour which it evolves will pass out from the neck under pressure expelling the air from the bulb. When the vapour has issued for some time and begins to escape more quietly, it may be kindled at the end of the tube, and the dropping of the flame will serve to indicate the moment at which the issue of vapour ceases. The end of the tube is then at once sealed by bringing a blowpipe flame to bear upon it. At this moment the temperature shown by the thermometer immersed in the bath and the barometric pressure are read.

The bulb is now removed from the bath, and is at once thoroughly dried and allowed to cool. It is then placed in the balance case for some time in order that it may assume the temperature of the air inside the case. The sealed bulb is then weighed and the temperature within the balance case is noted.

A file scratch is now made near the sealed end of the tube of the bulb, and the end is broken off under water which has been freed from air by having been recently boiled for some time and then rapidly cooled. The water will rush into the bulb. Any small air bubble must be carefully removed, if necessary, by warming the bulb by total immersion in hot water. The bulb is then cooled and weighed, and from the weight of water thus obtained the volume may be calculated.

435. Calculation of Results.—All the data for calculating the vapour density from the corrected volumes have now been obtained.

Let w_1 = weight of bulb full of air.
w_2 = weight of bulb full of vapour.
w_3 = weight of bulb full of water.

Then volume of flask is approximately

$$(w_3 - w_1) \text{ c.c.} = \text{V c.c., say,}$$

and the weight of air filling flask at ordinary temperature $t°$ and barometric pressure B

$$= \frac{\text{V} \times 0{\cdot}001293 \times 273 \times \text{B}}{(273 + t) \times 760} = w_4 \text{ gm., say.}$$

Hence weight of empty bulb

$$= w_1 - w_4 \text{ gm.,}$$

and weight of vapour filling bulb at temperature of bath T° and pressure B

$$= w_2 - (w_1 - w_4) \text{ gm.} = x \text{ gm.}$$

Weight of V c.c. of hydrogen at temperature T° and pressure B

$$= \frac{V \times 273 \times B \times 0{\cdot}00009}{(273 + T) \times 760} \text{ gm.}$$

$$= y \text{ gm.}$$

Hence vapour density $= \frac{x}{y}$.

NOTE.—Certain corrections of minor importance are omitted in the above calculation.

ESTIMATION OF TYPICAL GROUPS

440. In this section the more important methods for the estimation of typical groups are described, and a general method for the estimation of the relative amounts of ortho-, meta- and para-derivatives in a mixture is given. The following list indicates the type of compounds dealt with :—

	PAGE		PAGE
Acyl Compounds	306	Hydroxylic Compounds	309
Acids	307	Ethoxy- and Methoxy-Compounds	314
Alcohols	309	Ketones	310
Aldehydes	310	Nitro-Compounds	315
Amides	311	Phenols	309
Amines	311	Sugars	317
Azo-Compounds	314	Estimation of Ortho-, Meta- and Para-Compounds in a Mixture	321
Carboxyl Compounds	307		
Esters	306		

ESTIMATION OF ACYL GROUPS

441. Acyl compounds, such as formyl, acetyl and benzoyl derivatives of alcohols and phenols, may be estimated by—

(*a*) Hydrolysis with standard alkali, and the determination of the excess of alkali by titration (paragraph **442**).

(*b*) Hydrolysis with a non-volatile acid and steam-distillation of the volatile organic acid, which is then estimated by direct titration (paragraph **443**).

For the estimation of the acyl derivatives of amines, see paragraph **453**.

442. The acyl derivative is refluxed with alcoholic potash solution and the excess of alkali determined by titration.

Two similar flasks of about 200 c.c. capacity are fitted with reflux water condensers, using sound corks covered with smooth

tinfoil. Into each is pipetted 50 c.c. of alcoholic potassium hydroxide solution, approximately N/2. To one flask is then added a weighed quantity of the acyl derivative, roughly equivalent to half the alkali used.

The two flasks are gently refluxed on the water bath for about two hours and allowed to cool. The condensers are washed through with distilled water and the contents of the flasks separately titrated with standard sulphuric acid, approximately N/2, using phenolphthalein as an indicator. The difference between the two titrations gives the amount of alkali used in the saponification, and from this result the percentage of the acyl radical can be easily calculated. The hydrolysis of an acetyl derivative is represented by the equation :

$$R . OCOCH_3 + KOH \rightarrow R . OH + CH_3 . COOK$$

443. The acyl derivative is heated with benzene sulphonic acid and the organic acid removed by steam-distillation and determined in the distillate by direct titration.

Ten grams of benzene sulphonic acid are dissolved in about 100 c.c. of water and steam-distilled until the distillate is no longer acid in reaction. A weighed quantity of the acyl derivative, say, 0·5 gm., is then added to the flask containing the sulphonic acid, and the whole slowly steam-distilled until the liquid that passes over is neutral in reaction. It is advisable to use an "alkali-trap" between the distilling flask and the condenser to prevent the mechanical carrying over of the sulphonic acid.

The liberated organic acid present in the distillate is then titrated with N/10 barium hydroxide solution, using phenolphthalein as an indicator.

NOTE.—Other non-volatile acids, such as phosphoric acid and sulphuric acid, are sometimes used in place of benzene sulphonic acid. Phosphoric acid, however, is such a weak acid that hydrolysis of the acyl compound is very slow, and with sulphuric acid, there is always the risk of sulphur dioxide being produced by decomposition.

If benzene sulphonic acid is not available, the hydrolysis should be effected with alcoholic potash and an excess of phosphoric acid then added. The organic acid is then steam-distilled and titrated as described above.

THE ESTIMATION OF ACIDS

444. The estimation of the equivalent weight of an organic acid may be made by the following methods—

(*a*) By the silver salt method, described in paragraph **421.**

(*b*) By direct titration with alkali, free from carbonate, using phenolphthalein as an indicator, as described in paragraph **422.**

(*c*) By titration of the iodine liberated on the addition of potassium iodide and potassium iodate (paragraph **445**).

(*d*) By the analysis of the sodium, potassium, calcium, barium or copper salts (paragraph **446**).

445. The iodine liberated by the acid on the addition of a neutral solution of potassium iodide and iodate is estimated with a standard solution of sodium thiosulphate.

A weighed amount of the acid is added to an excess of a solution of potassium iodide and potassium iodate. If the acid is insoluble in water, then it is dissolved in alcohol, the iodide solution added, and the mixture shaken vigorously in a small stoppered bottle. If the substance be only a feeble acid, it is advisable to warm the stoppered bottle on the water bath to a temperature of 60°.

The liberated iodine is then titrated with standard thiosulphate solution using starch as an indicator:

$$6R\,.\,COOH + 5KI + KIO_3 \rightarrow 6R\,.\,COOK + 3I_2 + 3H_2O$$

446. The equivalent of the acid is determined by the analysis of one of its salts.

(*a*) *Silver Salt Method* (see paragraph **421**).

(*b*) *Sodium or Potassium Salt.*—The recrystallised alkali salt is dried in the air oven until constant in weight. About 0·5 gm. is then weighed out into a platinum or porcelain crucible and gently heated until decomposed. The residue is heated strongly over the blowpipe flame until all the carbon has been burnt away. This process is greatly facilitated by ignition in a slow current of oxygen.

The residue is allowed to cool and is then moistened with excess of dilute sulphuric acid, and the crucible is again heated, at first gently and then very strongly, until constant in weight. The crucible is now allowed to cool and 2 or 3 drops of sulphuric acid are added and the process repeated.

If a porcelain crucible is used especial care must be taken to ensure that all the acid sulphate is converted to the normal sulphate, a reaction that only takes place at a fairly high temperature.

From the weight of sodium sulphate obtained the equivalent of the acid is calculated.

(*c*) *Calcium and Barium Salts.*—Many organic acids form sparingly soluble salts of the alkaline earth metals, and these salts may be purified by recrystallisation from hot water. The salt used must afterwards be heated in the air oven to about 120° until constant in weight.

If the calcium salt is used, about 0·5 gm. of the dried salt is

heated very strongly in a porcelain or platinum crucible over the blowpipe flame, and the residue of calcium oxide weighed.

In the case of the barium salt about 0·4 gm. is weighed out, and the salt converted into the sulphate by means of sulphuric acid.

(*d*) *Copper Salt.*—Many amino-acids, such as glycine or anthranilic acid, form characteristic, sparingly soluble copper salts that may be recrystallised from hot water.

About 0·5 gm. of the dried salt is dissolved in boiling water and the copper estimated gravimetrically by precipitation as the oxide. In the case of organic acids, which prevent the precipitation of the copper oxide with sodium hydroxide, the copper salt is first ignited and the residue taken up in dilute nitric acid, filtering, if necessary, and then estimated as oxide. Alternatively, the copper may be precipitated as the sulphide, in the presence of organic acids.

THE ESTIMATION OF HYDROXYL GROUPS IN ALCOHOLS AND PHENOLS

447. The estimation of the hydroxyl group in alcohols and phenols may be made by :—

(*a*) Acetylation with acetic anhydride, and determination of the excess of the anhydride by titration (**448**).

(*b*) The preparation of a fully acetylated derivative, and the subsequent determination of the percentage of the acetyl group, as described in paragraphs **442**, **443**.

448. The hydroxylic compound is heated with acetic anhydride until fully acetylated, and the excess of the acid anhydride is determined by titration.

Weigh out carefully about 0·5 gm. of the compound, and place it in a small glass bottle having an accurately fitting stopper. By means of a dropping pipette add 2 c.c. of good acetic anhydride. In another similar bottle place 2 c.c. of the same acetic anhydride.

Partially immerse each bottle, both tightly stoppered, in boiling water for half an hour. Cool the bottles and add to each 50 c.c. of a normal solution of caustic soda. *Cool under the tap* and shake until all the excess of acetic anhydride has dissolved. If the undissolved reaction product is solid it should be well crushed, whilst in contact with the alkali, as it may enclose unneutralised acetic anhydride.

Titrate the contents of each bottle with decinormal hydrochloric or sulphuric acid, using phenolphthalein as an indicator. From

the difference between the readings calculate the weight of acetic anhydride that has reacted with the compound, and hence the number of hydroxyl groups in the compound.

THE ESTIMATION OF CARBONYL COMPOUNDS (ALDEHYDES AND KETONES)

449. Many volumetric methods have been described for the estimation of aldehydes and ketones. Gravimetric methods involving the precipitation of the para-bromphenylhydrazones and the para-nitrophenylhydrazones have also been fully treated. Unfortunately, the majority of these reactions do not yield accurate quantitative results with all aldehydes and ketones, and it is therefore necessary to choose a method that is applicable to the compound under examination.

Usually all aldehydes and methyl ketones which form stable addition products with $NaHSO_3$ may be estimated by Ripper's method, described in paragraph **450**, below, although aromatic hydroxy-aldehydes, such as salicylaldehyde, give results that are appreciably low.

In general, aromatic aldehydes are best estimated by the quantitative precipitation of the para-nitro- or para-bromphenylhydrazones, as described in paragraphs **451**, below.

For a detailed consideration of the relative methods for the quantitative determination of carbonyl compounds, see Feinberg, *Amer. Chem. J.*, 1913, **49**, 87.

450. Ripper's Method for the Estimation of Aldehydes.—This method is applicable to methyl ketones, such as acetone, that form relatively stable addition products with $NaHSO_3$.

The reaction depends upon the fact that the bisulphite addition compounds, unlike free sulphites, are not oxidised by a solution of iodine.

A solution of the aldehyde, about 0·5 per cent. in strength, in water or *very dilute* alcohol, is prepared. Solutions of decinormal iodine and of potassium bisulphite, about 12 gm. per litre, are also required.

Twenty-five cubic centimetres of the aldehyde solution is added to 50 c.c. of the bisulphite solution contained in a small stoppered bottle. The mixture is shaken and allowed to stand for a quarter of an hour. Meanwhile, 50 c.c. of the bisulphite solution is titrated with the decinormal iodine, using starch as an indicator:

$$R \cdot CHO + KHSO_3 \rightarrow R \cdot CH(OH) \cdot SO_3K$$

The excess of bisulphite in the aldehyde solution is then determined by means of the iodine solution. Then, if

A = weight of aldehyde in 25 c.c. of the solution,
M = molecular weight of the aldehyde,
and I = weight of iodine corresponding to the bisulphite that has combined with the aldehyde,

then $$A = \frac{I \times M}{254}.$$

451. The Gravimetric Estimation of Aldehydes by Precipitation as the Para-Nitrophenylhydrazone.—This process is particularly suitable for aromatic aldehydes, such as benzaldehyde, salicylaldehyde and vanillin, and also for acetone.

About 0·2 or 0·3 gm. of the aldehyde is weighed out and dissolved in 25 c.c. of 2N. acetic acid, and 50 c.c. of distilled water added. To this solution is added about twice the theoretical quantity of *p*-nitrophenylhydrazine dissolved in 30 c.c. of 30 per cent. acetic acid. The precipitation is complete after 4–5 hours. The precipitated hydrazone is filtered through a Gooch crucible and well washed with 2N. acetic acid, until the washings give but the faintest colour on the addition of alkali. The precipitate is dried at 110° until constant in weight.

THE ESTIMATION OF AMIDES

452. Amides are estimated by hydrolysis with acids or alkalis and the ammonia produced is determined by titration.

Hydrolysis by alkalies is effected by boiling a weighed quantity of the amide with a 10 per cent. solution of caustic soda, and the evolved ammonia is driven over directly into a known volume of standard acid:

$$R . CONH_2 + NaOH \rightarrow R . COONa + NH_3$$

In some cases it is better to hydrolyse with 50 per cent. sulphuric acid. The ammonia is then liberated by excess of alkali and distilled over and absorbed, as in the Kjeldahl process (paragraphs **401–403**).

A suitable apparatus for the distillation of the ammonia is shown in Fig. 33 (*b*), page 281.

THE ESTIMATION OF AMINES

453. Amines can be estimated by the following methods :—

(*a*) By the analysis of the salts formed with platinic chloride or with auric chloride. This method is suitable for *primary, secondary, and tertiary amines.*

(*b*) By titration with acids. Suitable for *aliphatic amines and some primary aromatic amines.*

(*c*) By acetylation with acetic anhydride, and determination of the excess of anhydride by titration. Suitable for *primary and secondary amines.*

(*d*) By acetylation and analysis of the acetyl derivative. Suitable for *primary and secondary amines.*

(*e*) By the measurement of the nitrogen evolved on interaction with nitrous acid. Suitable for *aliphatic primary amines.*

454. The Preparation and Analysis of Platinichlorides and Aurichlorides.—The estimation of organic bases by precipitation of the platinichloride has already been described in paragraph **423.** The aurichlorides, of general formula $B.HAuCl_4$, are similar, being well-crystallised salts readily obtained by the addition of a solution of auric chloride to the base dissolved in dilute hydrochloric acid. The weight of gold they contain is obtained by ignition.

455. The Titration of Amines.—Since the aliphatic amines are strong bases, they may be estimated by direct titration with standard hydrochloric or sulphuric acid, using methyl orange as an indicator. Aromatic amines are only feebly basic, and hence cannot be estimated in this way, although some can be titrated with special indicators, such as methyl red.

Primary aromatic amines react with nitrous acid in acid solution with the formation of diazonium compounds, and in some cases these amines can be estimated by titrating a solution of the hydrochloride of the base with a standard solution of sodium nitrite, using a starch-iodide paper as an indicator:

$$ArNH_2 + HONO + HCl \longrightarrow ArN : NCl + 2H_2O$$

In other cases the diazo-solution so produced is titrated with a standard solution of a naphthol until the two components no longer couple to form a dyestuff. Since these estimations are highly technical in nature, and in general each particular amine requires a specialised process, further information should be obtained by reference to standard works on the analysis of dyestuffs.

456. Primary and Secondary Amines are heated with an Excess of Acetic Anhydride, and the Excess of the Reagent determined by Titration.—The acetylation is carried out as described in paragraph **448.** In the case of secondary amines acetylation is difficult to accomplish and the heating should be continued for a longer period:

$$2R . NH_2 + (CH_3CO)_2O \longrightarrow 2RNH . COCH_3 + H_2O$$
$$2R_2 . NH + (CH_3 . CO)_2O \longrightarrow 2R_2 . N . COCH_3 + H_2O$$

The excess of acetic anhydride is then estimated as before (**448**).

457. Primary and Secondary Amines are acetylated or benzoy-

lated, and the resultant Acyl Derivative analysed.—The acyl derivative is recrystallised and dried. The derivative is then estimated as described in paragraphs **442**, **443**, but care must be taken to complete the reaction, as the acyl derivatives of amines are not as readily hydrolysed as those of hydroxylic compounds.

458. The Amount of Nitrogen evolved by the Interaction of Primary Aliphatic Amines and Nitrous Acid is measured.—About 0·2–0·5 gm. of the primary aliphatic amine is dissolved in three equivalents of normal hydrochloric acid contained in the flask *A* (Fig. 40). The apparatus is so arranged that the gases evolved on the addition of sodium nitrite solution are bubbled through a saturated solution of ferrous sulphate, and then through a solution of potassium permanganate containing sodium carbonate, and finally collected

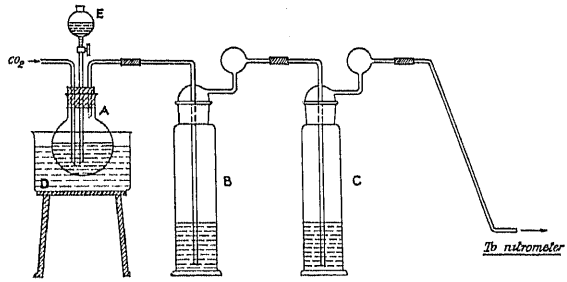


FIG. 40.—Estimation of Aliphatic Amines.

in a nitrometer containing a strong solution of potassium hydroxide (Fig. 32, page 278). The apparatus is arranged as in Fig. 40.

The air is first displaced from the apparatus by a current of carbon dioxide, free from air, prepared as described in paragraph **399**. The nitrometer is then connected and a saturated solution of three equivalents of sodium nitrite is run slowly into the flask by means of the tap funnel *E*:

$$R \cdot NH_2 + HNO_2 \rightarrow R \cdot OH + H_2O + N_2$$

After all the nitrite has been added, the flask *A* is heated to about 80° by immersion in a water bath *D*, and the gases passed through the absorption flasks by a slow current of carbon dioxide. The carbon dioxide is continued until all the bubbles of gas that pass into the nitrometer are absorbed.

The ferrous sulphate solution serves to absorb any nitric oxide evolved. The alkaline permanganate solution first oxidises and then absorbs any residual nitric oxide.

The volume of nitrogen in the nitrometer is noted, and the calculation made in the usual way, as described in paragraph **400**.

THE ESTIMATION OF AZO-COMPOUNDS

459. The azo-compounds are best estimated volumetrically with titanous chloride solution. Each azo-grouping requires 4 molecules of titanous chloride, the calculation being based on the equation :

$$ArN{=}NAr + 4TiCl_3 + 4HCl \rightarrow ArNH_2 + ArNH_2 + 4TiCl_4$$

The titanous chloride solution should be standardised by means of a decinormal solution of ferric alum, as described in paragraph **462**.

About 0·2 gm. of the azo-compound, dried in the air oven at 105°, is weighed out and boiled with an excess of the titanous chloride solution, a current of CO_2 being passed into the flask. After three minutes the solution is cooled under the tap and the excess of titanous chloride is estimated by direct titration with the solution of ferric alum, using potassium thiocyanate as an indicator. The process employed is the same as that for nitro-compounds, and is given in detail in paragraphs **461–463**.

THE ESTIMATION OF METHOXY AND ETHOXY GROUPS

460. Methoxy- and ethoxy- compounds are most conveniently estimated by Zeisel's Method, as modified by Perkin. The compound is heated with concentrated hydriodic acid and the alkyl

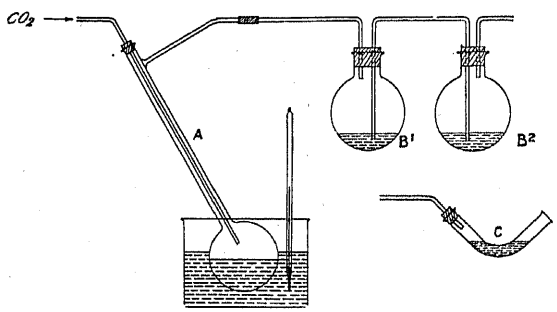


FIG. 41.—Zeisel Apparatus.

iodide so produced is carried over by a stream of carbon dioxide and absorbed in a solution of alcoholic silver nitrate. The silver iodide precipitated is then weighed :

$$R(OCH_3)_n + nHI \rightarrow R\,.\,(OH)_n + nCH_3I$$

Hydriodic Acid.—The hydriodic acid used must be the " constant boiling acid," B.P. 127°, and of density 1·7.

The decomposition of the compound is effected in a flask (*A*, Fig. 41) of about 30 c.c. capacity, with a neck not less than 8 inches long. The alkyl iodide is absorbed in two flasks B_1, B_2, each containing about 20 c.c. of alcoholic silver nitrate. The flask (*A*) is heated in a bath of glycerine.

About 0·3–0·35 gm. of the substance is weighed out and placed in *A*, and is covered with 15 c.c. of the hydriodic acid. A slow current of carbon dioxide is passed through the apparatus and the glycerine bath heated to 130–140°. When precipitation of the silver halide appears to have stopped the bath is heated until the hydriodic acid boils gently. At the end of an hour the absorption flasks are disconnected and a V-tube *C*, containing a little alcoholic silver nitrate substituted. The heating is then continued to about fifteen minutes to ensure that the reaction has been completed.

The contents of the absorption flasks are slowly poured into about 100 c.c. of hot water, acidified with nitric acid. The whole is boiled for some time until the alcohol has been driven off, and in order to decompose the stable double salt of silver iodide and nitrate that is formed in alcoholic solution. The silver iodide is then filtered and weighed in a Gooch crucible.

THE ESTIMATION OF NITRO-COMPOUNDS

461. Nitro-compounds are best estimated volumetrically with titanous chloride. It must be remembered that nitroso-, azo- and hydrazine compounds will also be reduced by this reagent:

$$ArNO_2 + 6HCl + 6TiCl_3 \rightarrow ArNH_2 + 2H_2O + 6TiCl_4$$

In all cases it is better to reduce the compound by boiling with an excess of titanous chloride, and then determine the residual titanous chloride by direct titration with ferric alum. It is necessary to store the titanous chloride in an atmosphere of carbon dioxide or hydrogen, and to carry out all titrations in a current of carbon dioxide.

462. The Titanous Chloride Solution.—The commercial solution of titanous chloride usually contains about 10–15 per cent. of $TiCl_3$. Sufficient of this solution to make about 2 litres of a decinormal solution is boiled with 200 c.c. of pure, strong hydrochloric acid and diluted to 1 litre. This solution is placed in the storage bottle *A* (Fig. 42), and about 10 gm. of zinc are added. This reduces any

titanic salts present. When the zinc has dissolved the solution is diluted to 2 litres with air-free distilled water. It is not permissible to reduce the solution with tin, since stannous chloride is also a reducing agent.

The storage vessel *A* is connected with a burette *B* as shown, and the latter is readily filled by means of the tap *C*. The whole apparatus is filled with carbon dioxide from a Kipp's apparatus connected at *G*, through the tube *F*, which leads to the bottom of the titanous chloride solution. The solution can be thoroughly mixed when required for use by opening the tap *E* and agitating the solution by a vigorous current of CO_2 from *F*.

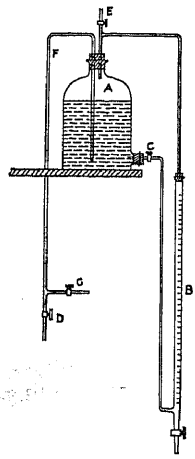


FIG. 42.—Apparatus for Titration with $TiCl_3$.

The titanous chloride solution is standardised by direct titration with a decinormal solution of ferric alum, containing free sulphuric acid. The titration is carried out in a conical flask, through which CO_2 is continually passed. The CO_2 for this purpose is obtained by a connection at the point *D*. Ten cubic centimetres of a strong solution of potassium thiocyanate are added as an indicator:

$$TiCl_3 + FeCl_3 \rightarrow TiCl_4 + FeCl_2$$

463. Estimation of the Nitro-Compound.—An approximately N/20 solution of the compound is prepared in water or dilute hydrochloric acid. If the substance is insoluble in dilute acid, then alcohol may be used as a solvent, but in this case a blank determination must be made in order to correct for impurities present in the alcohol. If the substance is insoluble in alcohol, it should first be sulphonated by warming with a little fuming sulphuric acid.

About 25 c.c. of the solution is measured into the titration flask and the current of CO_2 passed through. An excess, say 50 c.c., of $TiCl_3$ is then added and the mixture gently boiled for five minutes, the CO_2 being passed the whole time. The residual titanous chloride is then titrated with the ferric alum solution, with the addition of 10 c.c. of the strong solution of thiocyanate to act as an indicator.

It is always advisable, when great accuracy is required, to standardise the titanous chloride solution by means of a pure compound of the same type as that under examination.

THE ESTIMATION OF SUGARS

464. The sugars are usually estimated by one of the following methods :—

(*a*) With the polarimeter, by which the degree of optical activity is measured (**465**).

(*b*) Volumetrically, by the reduction of Fehling's solution (**466, 467**).

(*c*) Gravimetrically, by estimating the cuprous oxide precipitated from Fehling's solution (**468**).

465. Estimation by Means of the Polarimeter.—The use and adjustment of the polarimeter has been fully described on pages 19–22.

A solution of the sugar of definite strength, 10–20 per cent., is prepared and the degree of optical activity determined. If the solution is coloured or turbid it must be clarified by the use of one of the following agents :

(*a*) *Basic Lead Acetate Solution.*—This solution is prepared by grinding together in a mortar 10 gm. of lead monoxide and 25 gm. of normal lead acetate with a little water. The mass is washed into a beaker with sufficient distilled water to make about 100 c.c. altogether. The whole is boiled gently for half an hour and filtered.

(*b*) *Alumina Cream.*—This is prepared by pouring a hot solution of alum into a slight excess of a hot solution of sodium carbonate. The precipitated alumina is filtered off, well washed with boiling water, and then mixed in a mortar with sufficient water to form a smooth cream.

Process of Clarification.—A weighed quantity of the sugar is dissolved in distilled water in a graduated flask and a minimum quantity of the clarifying agent added. The whole is shaken violently for a few minutes and then the precipitate allowed to settle. The flask is now filled to the mark with water, any froth being destroyed by the addition of 2 or 3 drops of alcohol. The liquid is filtered through a dry filter paper the first portions being rejected.

In the case of exceptionally dark solutions it is sometimes necessary to bleach the solution with a little chlorine, subsequently destroying the excess of the reagent by the addition of a little sulphurous acid.

It is advisable that solutions of solid sugars, other than cane sugar, should be heated to boiling and then allowed to cool before use in the polarimeter. This is done in order to avoid errors due to bi-rotation. The presence of free acid does not affect the

optical activity of sugars, unless they are capable of "inversion," but any free alkali must be neutralised before polarimetric measurement.

The Inversion of Sugar.—The amount of cane sugar or sucrose present in a solution may be determined either directly or else after conversion into invert sugar by the agency of acids. This inversion is best accomplished by the addition of about 5 c.c. of pure hydrochloric acid to about 50 c.c. of the sugar solution. The mixture is warmed to 70° for fifteen minutes, allowed to cool, and is then made up to 100 c.c.

Since the degree of optical activity of the cane sugar is altered by inversion, this affords a valuable method of estimating cane sugar in a mixture of optically active substances, provided that the other active compounds are not affected by the acid. In this way the composition of a mixture of dextrose and cane sugar may be determined, the optical activity of the solution being measured both before and after inversion.

The Optical Activity of Sugars.—The specific rotation (**26**) of the more common sugars is given in the table below. The values for the more common optically active substances, other than the sugars, are given in the tables of properties in the qualitative section.

Sugar.	$[\alpha]_D^{15°}$	Sugar	$[\alpha]_D^{15°}$
Arabinose $C_5H_{10}O_5$	+ 104·5°	Lævulose (Fructose) $C_6H_{12}O_6$	− 92·5°
Dextrose (Glucose) $C_6H_{12}O_6$	+ 52·8°	Maltose (Malt Sugar) $C_{12}H_{22}O_{11} + H_2O$	+ 137·8°
Galactose $C_6H_{12}O_6$	+ 81·0°	Sucrose (Cane Sugar) $C_{12}H_{22}O_{11}$	+ 66·5°
Lactose (Milk Sugar) $C_{12}H_{22}O_{11} + H_2O$	+ 52·5°	Invert Sugar $C_6H_{12}O_6 + C_6H_{12}O_6$	− 19·8°

466. The Volumetric Estimation of Sugars by Fehling's Solution.—Fehling's solution is prepared by mixing when required, equal volumes of the two following solutions :

Fehling's Solution I.—34·64 gm. of recrystallised copper sulphate is dissolved in 500 c.c. of distilled water containing a few drops of sulphuric acid.

Fehling's Solution II.—60 gm. of pure caustic soda and 173 gm. of Rochelle salt (sodium potassium tartrate) are dissolved in 500 c.c. of distilled water.

Standardisation of the Fehling's Solution.—A one per cent. solution of pure dextrose is prepared from the sugar previously dried over sulphuric acid in a vacuum desiccator for twenty-four hours. Twenty or twenty-five c.c. of the Fehling's solution is run into a conical flask and diluted with air-free distilled water to a mark made on the flask (about 50 c.c.). The solution is boiled and the dextrose solution run in from a burette until the blue colour of the solution disappears. This approximate determination having been made, the process is repeated carefully as follows. The Fehling's solution is boiled and the solution of glucose run in to within 2 c.c. of the end-point. The mixture is boiled for one minute and a further 1·5 c.c. added. The mixture is again boiled for a minute and the sugar solution added drop by drop until the blue colour of the solution disappears. The end-point may be seen if the heavy precipitate of cuprous oxide is allowed to settle, or by the use of a solution of potassium ferrocyanide in dilute acetic acid, as an external indicator. One drop of the titrated solution is allowed to filter through a very small filter paper on to a white tile so that it just touches a spot of the indicator. If the titration is incomplete a brown precipitate of copper ferrocyanide is formed as a fringe at the junction of the liquids.

Each cubic centimetre of a solution prepared exactly as described above should be equivalent to 0·005 gm. of dextrose.

One cubic centimetre of such a solution is equivalent to—

0·005 gm. dextrose, lævulose or invert sugar.
0·00475 gm. cane sugar after inversion.
0·00675 gm. lactose.
0·00805 gm. maltose.

In all estimations the exact conditions used in standardising the solution must be rigidly adhered to. Cane sugar must be inverted (see page 318) before use.

467. The Volumetric Estimation of Sugars by Fehling's Solution, as modified by Pavy.—In this process the titration is carried out in the presence of ammonia so that the cuprous oxide is not precipitated, but forms a colourless solution, and the end of the reaction is indicated by the complete decolorisation of the blue solution. As the ammoniacal cuprous solution is very easily oxidised it is necessary to avoid access of air. The titration is carried out in a conical flask provided with a cork bored with two holes. Through

one hole is placed a long piece of glass tubing that acts as a reflux air condenser. Through the other a small piece of glass tubing is passed, which is attached by rubber tubing to the burette containing the sugar solution. More accurate results are obtained if a slow current of coal gas is passed into the flask by means of a third tube.

The solution is prepared by diluting about 120 c.c. of the ordinary Fehling's solution with 300 c.c. of strong ammonia and 400 c.c. of caustic soda solution containing 50 gm. of sodium hydroxide, the whole solution is then made up to 1 litre. For each titration 100 c.c. of this solution is used. It is standardised by means of dextrose.

The solution is boiled slowly in the flask which contains a few pieces of broken porcelain to minimise bumping. The sugar solution is run in slowly, the boiling being continued regularly. The end-point is well defined, but the reduction is slower than with the ordinary Fehling's solution.

468. The Gravimetric Estimation of Sugars by Means of Fehling's Solution.—In this process the cuprous oxide precipitated on boiling a solution of the sugar with an excess of Fehling's solution is filtered off, redissolved, precipitated and weighed as cupric oxide. The direct weighing of the cuprous oxide, although sometimes adopted, is not very satisfactory. The precipitated cuprous oxide may also be estimated as cuprous thiocyanate. Cane sugar and malt sugar must be inverted before estimation.

A known volume of the sugar solution is inverted if necessary, and heated on the water bath for fifteen minutes with an excess of Fehling's solution. The precipitated cuprous oxide is filtered off by suction and well washed with hot water. The precipitate is then dissolved in dilute nitric acid and the copper precipitated from the boiling solution by the addition of an excess of sodium hydroxide. The cupric oxide is estimated gravimetrically in the usual manner—

1 gm. CuO = 0·4535 gm. dextrose, lævulose or invert sugar.
= 0·4308 gm. cane sugar after inversion.
= 0·6153 gm. lactose.
= 0·7314 gm. maltose.

THE DETERMINATION OF THE RELATIVE AMOUNTS OF ORTHO-, META-, AND PARA-ISOMERS IN A MIXTURE

469. It is usually assumed that di-substitution in the benzene nucleus results in the formation of either the meta-compound, or else a mixture of the ortho- and para-isomers. In nearly every case, however, all three compounds are produced, but either the meta- predominates or else a mixture of the ortho- and para-. It is often of importance to be able to determine the amount of each product formed on di-substitution, but, unfortunately, there is no general method known by which this can be done rapidly. In one or two particular cases the relative amount of one isomer may be determined by chemical reaction, as in the case of the nitro-halogen-benzenes. In this case the mixture is heated with alkalies under pressure and the halogen atom in the ortho- and para-compounds is replaced, and alkali halide formed. The meta-compound does not react.

$$o\text{- or } p\text{-Cl} \cdot C_6N_4 \cdot NO_2 + KOH \rightarrow HO \cdot C_6H_4 \cdot NO_2 + KCl$$

Hence the estimation of the meta-compound in the mixture is made by determining what percentage of the halogen can be removed with alkalies and afterwards precipitated as the silver salt.

In a somewhat similar way the estimation of one of the constituents in a mixture may be determined when only one of the compounds is steam-volatile, and can be removed in this way, as is the case with ortho-nitrophenol.

METHODS OF GENERAL APPLICATION

470. (*a*) *Solubility Method.*—In this process any one of three position isomers can be removed by repeated extraction of the mixture with a solvent previously saturated with the other two isomers. Thus the nitrobenzoic acids may be separated by aqueous extraction. The amount of the meta-compound in the mixture is determined by repeated extraction of the mass with water already saturated with the ortho- and para-nitrobenzoic acids, and so on. This method is somewhat unsatisfactory in that an absolutely constant temperature must be maintained throughout the operations. Thus, if the temperature of the extracting solvent cools during the process of extraction, then some of the ortho- and para-compounds would be

thrown out of the solution. On the other hand, if the temperature increases the solvent would be no longer saturated with these two compounds.

(*b*) *Freezing Point Method.*—Since the three isomerides have the same molecular weight, equal quantities will depress the freezing-point of a solvent to the same extent. Hence the relative amount of the meta-isomer in a mixture can be made by comparing the depression of the freezing-point produced on the addition of a known weight of the mixture to some of the pure meta-compound used as a solvent, with the depression produced on the addition of the same weight of the pure ortho- or para-compound. Thus, if the addition of 1 gm. of the mixture to 20 gm. of the pure meta-compound gave a depression of the freezing-point of 2° C., and if the addition of 1 gm. of the pure ortho- or para-compound to the same weight of meta- gave a depression of 3° C., obviously the amount of meta-compound present is one-third of the whole. Similarly, the relative amounts of the ortho- and para-substances can be obtained.

This method is of general application. It should be remembered that—

(*a*) *The depression of the freezing-point of the meta-compound used as a solvent is due solely to the ortho- and para- added.*

(*b*) *The depression of the freezing-point of the ortho-compound when used as a solvent is due solely to the meta- and para- added.*

(*c*) *The depression of the freezing-point of the para-compound when used as a solvent is due solely to the ortho- and meta- added.*

The depressions of the freezing-points can be determined quite conveniently, and with sufficient accuracy, by the method described on page 11 for the determination of setting-point.

APPENDIX

500. Table of Atomic Weights as Issued by the International Union of Pure and Applied Chemistry, 1925.

	Symbol.	Atomic No.	Atomic Weight.		Symbol.	Atomic No.	Atomic Weight.
Aluminium	Al	13	26·97	Mercury	Hg	80	200·61
Antimony	Sb	51	121·77	Molybdenum	Mo	42	96·0
Argon	A	18	39·91	Neodymium	Nd	60	144·27
Arsenic	As	33	74·96	Neon	Ne	10	20·2
Barium	Ba	56	137·37	Nickel	Ni	28	58·69
Beryllium	Be	4	9·02	Nitrogen	N	7	14·008
Glucinium	Gl			Osmium	Os	76	190·8
Bismuth	Bi	83	209·00	Oxygen	O	8	16·000
Boron	B	5	10·82	Palladium	Pd	46	106·7
Bromine	Br	35	79·916	Phosphorus	P	15	31·027
Cadmium	Cd	48	112·41	Platinum	Pt	78	195·23
Cæsium	Cs	55	132·81	Potassium	K	19	39·096
Calcium	Ca	20	40·07	Praseodymium	Pr	59	140·92
Carbon	C	6	12·000	Radium	Ra	88	225·95
Cerium	Ce	58	140·25	Radon	Rn	86	222·0
Chlorine	Cl	17	35·457	Rhodium	Rh	45	102·91
Chromium	Cr	24	52·01	Rubidium	Rb	37	85·44
Cobalt	Co	27	58·94	Ruthenium	Ru	44	101·7
Columbium	Cb	41	93·1	Samarium	Sm	62	150·43
Niobium	Nb			Scandium	Sc	21	45·10
Copper	Cu	29	63·57	Selenium	Se	34	79·2
Dysprosium	Dy	66	162·52	Silicon	Si	14	28·06
Erbium	Er	68	167·7	Silver	Ag	47	107·880
Europium	Eu	63	152·0	Sodium	Na	11	22.997
Fluorine	F	9	19·00	Strontium	Sr	38	87·63
Gadolinium	Gd	64	157·26	Sulphur	S	16	32·064
Gallium	Ga	31	69·72	Tantalum	Ta	73	181·5
Germanium	Ge	32	72·60	Tellurium	Te	52	127·5
Gold	Au	79	197·2	Terbium	Tb	65	159·2
Helium	He	2	4·00	Thallium	Tl	81	204·39
Holmium	Ho	67	163·4	Thorium	Th	90	232·15
Hydrogen	H	1	1·008	Thulium	Tm	69	169·4
Indium	In	49	114·8	Tin	Sn	50	118·70
Iodine	I	53	126·932	Titanium	Ti	22	48·1
Iridium	Ir	77	193·1	Tungsten	W	76	184·0
Iron	Fe	26	55·84	Wolfram			
Krypton	Kr	36	82·9	Uranium	U	92	238·17
Lanthanum	La	57	138·90	Vanadium	V	23	50·96
Lead	Pb	82	207·20	Xenon	Xe	54	130·2
Lithium	Li	3	6·940	Ytterbium	Yb	70	173·6
Lutecium	Lu	71	175·0	Yttrium	Y	39	88·9
Magnesium	Mg	12	24·32	Zinc	Zn	30	65·38
Manganese	Mn	25	54·93	Zirconium	Zr	40	91·0

501. Expansion of Water.

(Kopp).

Temperature, Centigrade	Volume (Volume at 0°=1).	Density (Density at 0°=1).	Volume (Volume at 4°=1).	Density (Density at 4°=1).
0	1·00000	1·000000	1·00012	0·999877
1	0·99995	1·000053	1·00007	0·999930
2	0·99991	1·000092	1·00003	0·999969
3	0·99989	1·000115	1·00001	0·999992
4	0·99988	1·000123	1·00000	1·000000
5	0·99988	1·000117	1·00001	0·999994
6	0·99990	1·000097	1·00003	0·999973
7	0·99994	1·000062	1·00006	0·999939
8	0·99999	1·000014	1·00011	0·999890
9	1·00005	0·999952	1·00017	0·999829
10	1·00012	0·999876	1·00025	0·999753
11	1·00021	0·999785	1·00034	0·999664
12	1·00031	0·999686	1·00044	0·999562
13	1·00043	0·999572	1·00055	0.999449
14	1·00056	0·999445	1·00068	0·999322
15	1 00070	0·999306	1·00082	0·999183
16	1·00085	0·999155	1·00097	0·999032
17	1·00101	0·998992	1·00113	0·998869
18	1·00118	0·998817	1·00131	0·998695
19	1·00137	0·998631	1·00149	0·998509
20	1·00157	0·998435	1·00169	0·998312
21	1·00178	0·998228	1·00190	0·998104
22	1·00200	0·998010	1·00212	0·997886
23	1·00223	0·997780	1·00235	0·997657
24	1·00247	0·997541	1·00259	0·997419
25	1·00271	0·997293	1·00284	0·997170
26	1·00295	0·997035	1·00310	0·996912
27	1·00319	0·996767	1·00337	0·996644
28	1·00347	0·996489	1·00365	0·996367
29	1·00376	0·996202	1·00393	0·996082
30	1·00406	0·996008	1·00423	0·995787

502. Pressure of Aqueous Vapour for each Tenth of a Degree Centigrade from 0° to 30° C.

(Regnault).

Temp. C.	Press^{e}. in mm. of Mercury.	Temp. C.	Press^{e}. in mm. of Mercury.	Temp. C.	Press^{e}. in mm. of Mercury.	Temp. C.	Press^{e}. in mm. of Mercury.	Temp. C.	Press^{e}. in mm. of Mercury.
0·0	4·6	6·0	7·0	12·0	10·5	18·0	15·4	24·0	22·2
·1	4·6	·1	7·0	·1	10·5	·1	15·5	·1	22·3
·2	4·7	·2	7·1	·2	10·6	·2	15·6	·2	22·5
·3	4·7	·3	7·1	·3	10·7	·3	15·7	·3	22·6
·4	4·7	·4	7·2	·4	10·7	·4	15·7	·4	22·7
·5	4·8	·5	7·2	·5	10·8	·5	15·8	·5	22·9
·6	4·8	·6	7·3	·6	10·9	·6	15·9	·6	23·0
·7	4·9	·7	7·3	·7	10·9	·7	16·0	·7	23·1
·8	4·9	·8	7·4	·8	11·0	·8	16·1	·8	23·3
·9	4·9	·9	7·4	·9	11·1	·9	16·2	·9	23·4
1·0	4·9	7·0	7·5	13·0	11·2	19·0	16·3	25·0	23·5
·1	5·0	·1	7·5	·1	11·2	·1	16·4	·1	23·7
·2	5·0	·2	7·6	·2	11·3	·2	16·6	·2	23·8
·3	5·0	·3	7·6	·3	11·4	·3	16·7	·3	24·0
·4	5·1	·4	7·7	·4	11·5	·4	16·8	·4	24·1
·5	5·1	·5	7·8	·5	11·5	·5	16·9	·5	24·3
·6	5·2	·6	7·8	·6	11·6	·6	17·0	·6	24·4
·7	5·2	·7	7·9	·7	11·7	·7	17·1	·7	24·6
·8	5·2	·8	7·9	·8	11·8	·8	17·2	·8	24·7
·9	5·3	·9	8·0	·9	11·8	·9	17·3	·9	24·8
2·0	5·3	8·0	8·0	14·0	11·9	20·0	17·4	26·0	25·0
·1	5·3	·1	8·1	·1	12·0	·1	17·5	·1	25·1
·2	5·4	·2	8·1	·2	12·1	·2	17·6	·2	25·3
·3	5·4	·3	8·2	·3	12·1	·3	17·7	·3	25·4
·4	5·5	·4	8·2	·4	12·2	·4	17·8	·4	25·6
·5	5·5	·5	8·3	·5	12·3	5	17·9	·5	25·7
·6	5·5	·6	8·3	·6	12·4	·6	18·0	·6	25·9
·7	5·6	·7	8·4	·7	12·5	·7	18·2	·7	26·0
·8	5·6	·8	8·5	·8	12·5	·8	18·3	·8	26·2
·9	5·6	·9	8·5	·9	12·6	·9	18·4	·9	26·4
3·0	5·7	9·0	8·6	15·0	12·7	21·0	18·5	27·0	26·5
·1	5·7	·1	8·6	·1	12·8	·1	18·6	·1	26·7
·2	5·8	·2	8·7	·2	12·9	·2	18·7	·2	26·8
·3	5·8	·3	8·7	·3	12·9	·3	18·8	·3	27·0
·4	5·8	·4	8·8	·4	13·0	·4	19·0	·4	27·1
·5	5·9	·5	8·9	·5	13·1	·5	19·1	·5	27·3
·6	5·9	·6	8·9	·6	13·2	·6	19·2	·6	27·5
·7	6·0	·7	9·0	·7	13·3	·7	19·3	·7	27·6
·8	6·0	·8	9·0	·8	13·4	·8	19·4	·8	27·8
·9	6·1	·9	9·1	·9	13·5	·9	19·5	·9	27·9
4·0	6·1	10·0	9·2	16·0	13·5	22·0	19·7	28·0	28·1
·1	6·1	·1	9·2	·1	13·6	·1	19·8	·1	28·3
·2	6·2	·2	9·3	·2	13·7	·2	19·9	·2	28·4
·3	6·2	·3	9·3	·3	13·8	·3	20·0	·3	28·6
·4	6·3	·4	9·4	·4	13·9	·4	20·1	·4	28·8
·5	6·3	·5	9·5	·5	14·0	·5	20·3	·5	28·9
·6	6·4	·6	9·5	·6	14·1	·6	20·4	·6	29·1
·7	6·4	·7	9·6	·7	14·2	·7	20·5	·7	29·3
·8	6·4	·8	9·7	·8	14·2	·8	20·6	·8	29·4
·9	6·5	·9	9·7	·9	14·3	·9	20·8	·9	29·6
5·0	6·5	11·0	9·8	17·0	14·4	23·0	20·9	29·0	29·8
·1	6·6	·1	9·9	·1	14·5	·1	21·0	·1	30·0
·2	6·6	·2	9·9	·2	14·6	·2	21·1	·2	30·1
·3	6·7	·3	10·0	·3	14·7	·3	21·3	·3	30·3
·4	6·7	·4	10·1	·4	14·8	·4	21·4	·4	30·5
·5	6·8	·5	10·1	·5	14·9	·5	21·5	·5	30·7
·6	6·8	·6	10·2	·6	15·0	·6	21·7	·6	30·8
·7	6·9	·7	10·3	·7	15·1	·7	21·8	·7	31·0
·8	6·9	·8	10·3	·8	15·2	·8	21·9	·8	31·2
·9	7·0	·9	10·4	·9	15·3	·9	22·1	·9	31·4

503. WEIGHT IN MILLIGRAMS OF 1 C.C. OF MOIST NITROGEN UNDER

Pressure in

$t°$	730	732	734	736	738	740	742	744	746	748
10°	1·144	1·147	1·151	1·154	1·157	1·160	1·163	1·166	1·170	1·173
11°	1·139	1·142	1·145	1·149	1·152	1·155	1·158	1·161	1·164	1·168
12°	1·134	1·137	1·140	1·144	1·147	1·150	1·153	1·156	1·159	1·163
13°	1·129	1·132	1·135	1·139	1·142	1·145	1·148	1·151	1·154	1·157
14°	1·124	1·127	1·130	1·133	1·136	1·140	1·143	1·146	1·149	1·152
15°	1·119	1·122	1·125	1·128	1·131	1·134	1·137	1·141	1·144	1·147
16°	1·114	1·117	1·120	1·123	1·126	1·129	1·132	1·135	1·138	1·142
17°	1·108	1·111	1·115	1·118	1·121	1·124	1·127	1·130	1·133	1·136
18°	1·103	1·106	1·109	1·112	1·116	1·119	1·122	1·125	1·128	1·131
19°	1·098	1·101	1·104	1·107	1·110	1·113	1·116	1·119	1·122	1·126
20°	1·092	1·095	1·099	1·102	1·105	1·108	1·111	1·114	1·117	1·120
21°	1·087	1·090	1·093	1·096	1·099	1·102	1·105	1·108	1·111	1·115
22°	1·082	1·085	1·088	1·091	1·094	1·097	1·100	1·103	1·106	1·109
23°	1·076	1·079	1·082	1·085	1·088	1·091	1·094	1·097	1·100	1·103
24°	1·070	1·073	1·076	1·080	1·083	1·086	1·089	1·092	1·095	1·098
25°	1·065	1·068	1·071	1·074	1·077	1·080	1·083	1·086	1·089	1·092

Various Conditions of Temperature and Pressure.

Millimetres.

750	752	754	756	758	760	762	764	766	768	770	$t°$
1·176	1·179	1·182	1·186	1·189	1·192	1·195	1·198	1·201	1·205	1·208	10°
1·171	1·174	1·177	1·180	1·183	1·187	1·190	1·193	1·196	1·199	1·202	11°
1·166	1·169	1·172	1·175	1·178	1·181	1·185	1·188	1·191	1·194	1·197	12°
1·161	1·164	1·167	1·170	1·173	1·176	1·179	1·182	1·186	1·189	1·192	13°
1·155	1·158	1·161	1·165	1·168	1·171	1·174	1·177	1·180	1·183	1·187	14°
1·150	1·153	1·156	1·159	1·162	1·166	1·169	1·172	1·175	1·178	1·181	15°
1·145	1·148	1·151	1·154	1·157	1·160	1·163	1·166	1·170	1·173	1·176	16°
1·139	1·142	1·146	1·149	1·152	1·155	1·158	1·161	1·164	1·167	1·170	17°
1·134	1·137	1·140	1·143	1·146	1·149	1·153	1·156	1·159	1·162	1·165	18°
1·129	1·132	1·135	1·138	1·141	1·144	1·147	1·150	1·153	1·156	1·159	19°
1·123	1·126	1·129	1·132	1·135	1·138	1·141	1·145	1·148	1·151	1·154	20°
1·118	1·121	1·124	1·127	1·130	1·133	1·136	1·139	1·142	1·145	1·148	21°
1·112	1·115	1·118	1·121	1·124	1·127	1·130	1·133	1·136	1·139	1·143	22°
1·106	1·109	1·112	1·115	1·119	1·122	1·125	1·128	1·131	1·134	1·137	23°
1·101	1·104	1·107	1·110	1·113	1·116	1·119	1·122	1·125	1·128	1·131	24°
1·095	1·098	1·101	1·104	1·107	1·110	1·113	1·116	1·119	1·122	1·125	25°

504. PERCENTAGE OF ABSOLUTE ALCOHOL, C_2H_5OH, BY WEIGHT AND BY VOLUME, CORRESPONDING TO THE SPECIFIC GRAVITY TAKEN AT 60° F. OR 15·6° C. WATER = 1.

Specific Gravity.	Percentage of C_2H_5OH.		Specific Gravity.	Percentage of C_2H_5OH.		Specific Gravity.	Percentage of C_2H_5OH.		Specific Gravity.	Percentage of C_2H_5OH.	
	By Weight.	By Volume at 60° F.		By Weight.	By Volume at 60° F.		By Weight.	By Volume at 60° F.		By Weight.	By Volume at 60° F.
0·794	99·87	99·92	0·847	80·39	85·80	0·900	58·06	65·83	0·953	32·67	39·22
0·795	99·55	99·72	0·848	79·98	85·46	0·901	57·62	65·41	0·954	32·09	38·57
0·796	99·22	99·52	0·849	79·58	85·12	0·902	57·18	64·98	0·955	31·50	37·89
0·797	98·90	99·32	0·850	79·17	84·78	0·903	56·75	64·56	0·956	30·90	37·20
0·798	98·57	99·12	0·851	78·76	84·44	0·904	56·31	64·13	0·957	30·28	36·50
0·799	98·24	98·91	0·852	78·35	84·11	0·905	55·87	63·70	0·958	29·66	35·79
0·800	97·91	98·70	0·853	77·94	83·77	0·906	55·42	63·26	0·959	29·03	35·06
0·801	97·59	98·49	0·854	77·53	83·42	0·907	54·98	62·83	0·960	28·39	34·33
0·802	97·25	98·28	0·855	77·12	83·08	0·908	54·54	62·39	0·961	27·73	33·56
0·803	96·91	98·06	0·856	76·71	82·73	0 909	54·10	61·95	0·962	27·06	32·79
0·804	96·57	97·84	0·857	76·30	82·38	0·910	53·65	61·51	0·963	26·37	31·99
0·805	96·23	97·62	0·858	75·88	82·03	0·911	53·21	61·07	0·964	25·68	31·18
0·806	95·89	97·39	0·859	75·47	81·68	0·912	52·77	60·63	0·965	24·97	30·34
0·807	95·55	97·16	0·860	75·05	81·32	0·913	52·33	60·19	0·966	24·23	29·48
0·808	95·20	96·93	0·861	74·64	80·97	0·914	51·88	59·74	0·967	23·48	28·60
0·809	94·85	96·69	0·862	74·22	80·61	0·915	51·43	59·29	0·968	22·71	27·69
0·810	94·50	96·45	0·863	73·81	80·25	0·916	50·98	58·83	0·969	21·93	26·77
0·811	94·15	96·21	0·864	73·39	79·89	0·917	50·53	58·38	0·970	21·14	25·83
0·812	93·80	95·97	0·865	72·97	79·53	0·918	50·08	57·92	0·971	20·34	24·85
0·813	93·44	95·72	0·866	72·55	79·16	0·919	49·63	57·46	0·972	19·53	23·91
0·814	93·08	95·47	0·867	72·14	78·80	0·920	49·17	56·99	0·973	18·72	22·94
0·815	92·72	95·22	0·868	71·72	78·43	0·921	48·71	56·52	0·974	17·90	21·96
0·816	92·36	94·97	0·869	71·30	78·06	0·922	48·25	56·05	0·975	17·08	20·97
0·817	92·00	94·71	0·870	70·88	77·69	0·923	47·79	55·58	0·976	16·25	19·98
0·818	91·63	94·45	0·871	70·46	77·32	0·924	47·33	55·10	0·977	15·43	18·99
0·819	91·27	94·19	0·872	70·04	76·94	0·925	46·87	54·62	0·978	14·61	18·00
0·820	90·90	93·92	0·873	69·62	76·57	0·926	46·40	54·14	0·979	13·80	17·02
0·821	90·53	93·65	0·874	69·19	76·19	0·927	45·94	53·65	0·980	12·99	16·04
0·822	90·16	93·38	0·875	68·77	75·82	0·928	45·47	53·16	0·981	12·20	15·08
0·823	89·79	93·11	0·876	68·35	75·44	0·929	45·00	52·67	0·982	11·42	14·13
0·824	89·41	92·83	0·877	67·93	75·06	0·930	44·53	52·18	0·983	10·65	13·20
0·825	89·03	92·55	0·878	67·51	74·68	0·931	44·06	51·68	0·984	9·91	12·29
0·826	88·65	92·26	0·879	67·09	74·30	0·932	43·59	51·18	0·985	9·18	11·40
0·827	88·27	91·98	0·880	66·66	73·91	0·933	43·11	50·67	0·986	8·46	10·51
0·828	87·88	91·69	0·881	66·24	73·52	0·934	42·62	50·15	0·987	7·76	9·65
0·829	87·50	91·40	0·882	65·81	73·13	0·935	42·13	49·63	0·988	7·08	8·80
0·830	87·11	91·11	0·883	65·39	72·74	0·936	41·64	49·10	0·989	6·41	7·98
0·831	86·73	90·82	0·884	64·96	72·34	0·937	41·15	48·57	0·990	5·76	7·18
0·832	86·34	90·52	0·885	64·53	71·95	0·938	40·65	48·04	0·991	5·13	6·40
0·833	85·95	90·22	0·886	64·10	71·55	0·939	40·15	47·50	0·992	4·51	5·63
0·834	85·56	89·91	0·887	63·67	71·15	0·940	39·65	46·95	0·993	3·90	4·88
0·835	85·17	89·61	0·888	63·24	70·75	0·941	39·15	46·40	0·994	3·31	4·14
0·836	84·78	89·30	0·889	62·81	70·35	0·942	38·64	45·85	0·995	2·73	3·42
0·837	84·39	88·99	0·890	62·38	69·95	0·943	38·12	45·28	0·996	2·17	2·71
0·838	83·99	88·68	0·891	61·95	69·55	0·944	37·60	44·71	0·997	1·61	2·02
0·839	83·60	88·37	0·892	61·52	69·14	0·945	37·07	44·13	0·998	1·07	1·34
0·840	83·20	88·06	0·893	61·09	68·74	0·946	36·54	43·54	0·999	0·53	0·66
0·841	82·80	87·74	0·894	60·66	68·33	0·947	36·00	42·95	—	—	—
0·842	82·40	87·42	0·895	60·23	67·92	0·948	35·46	42·35	—	—	—
0·843	82·00	87·09	0·896	59·80	67·50	0·949	34·92	41·74	—	—	—
0·844	81·60	86·77	0·897	59·37	67·08	0·950	34·37	41·13	—	—	—
0·845	81·20	86·44	0·898	58·93	66·67	0·951	33·81	40·50	—	—	—
0·846	80·79	86·12	0·899	58·50	66·25	0·952	33·25	39·87	—	—	—

SULPHURIC ACID.

505. PERCENTAGE BY WEIGHT OF H_2SO_4 PRESENT IN AQUEOUS SOLUTION OF KNOWN SPECIFIC GRAVITY AT 15·5° C.

(Lunge and Isler.)

Specific Gravity.	Percentage of H_2SO_4.	Specific Gravity.	Percentage of H_2SO_4.	Specific Gravity.	Percentage of H_2SO_4.
1·005	0·83	1·190	26·04	1·375	47·47
1·010	1·57	1·195	26·68	1·380	48·00
1·015	2·30	1·200	27·32	1·385	48·53
1·020	3·03	1·205	27·95	1·390	49·06
1·025	3·76	1·210	28·58	1·395	49·59
1·030	4·49	1·215	29·21	1·400	50·11
1·035	5·23	1·220	29·84	1·405	50·63
1·040	5·96	1·225	30·48	1·410	51·15
1·045	6·67	1·230	31·11	1·415	51·66
1·050	7·37	1·235	31·70	1·420	52·15
1·055	8·07	1·240	32·28	1·425	52·63
1·060	8·77	1·245	32·86	1·430	53·11
1·065	9·47	1·250	33·43	1·435	53·59
1·070	10·19	1·255	34·00	1·440	54·07
1·075	10·90	1·260	34·57	1·445	54·55
1·080	11·60	1·265	35·14	1·450	55·03
1·085	12·30	1·270	35·71	1·455	55·50
1·090	12·99	1·275	36·29	1·460	55·97
1·095	13·67	1·280	36·87	1·465	56·43
1·100	14·35	1·285	37·45	1·470	56·90
1·105	15·03	1·290	38·03	1·475	57·37
1·110	15·71	1·295	38·61	1·480	57·83
1·115	16·36	1·300	39·19	1·485	58·28
1·120	17·01	1·305	39·77	1·490	58·74
1·125	17·66	1·310	40·35	1·495	59·22
1·130	18·31	1·315	40·93	1·500	59·70
1·135	18·96	1·320	41·50	1·505	60·18
1·140	19·61	1·325	42·08	1·510	60·65
1·145	20·26	1·330	42·66	1·515	61·12
1·150	20·91	1·335	43·20	1·520	61·59
1·155	21·55	1·340	43·74	1·525	62·06
1·160	22·19	1·345	44·28	1·530	62·53
1·165	22·83	1·350	44·82	1·535	63·00
1·170	23·47	1·355	45·35	1·540	63·43
1·175	24·12	1·360	45·88	1·545	63·85
1·180	24·76	1·365	46·41	1·550	64·26
1·185	25·40	1·370	46·94	1·555	64·67

505. SULPHURIC ACID (*continued*).

Specific Gravity.	Percentage of H_2SO_4.	Specific Gravity.	Percentage of H_2SO_4.	Specific Gravity.	Percentage of H_2SO_4.
1·560	65·08	1·700	77·17	1·823	90·60
1·565	65·49	1·705	77·60	1·824	90·80
1·570	65·90	1·710	78·04	1·825	91·00
1·575	66·30	1·715	78·48	1·826	91·25
1·580	66·71	1·720	78·92	1·827	91·50
1·585	67·13	1·725	79·36	1·828	91·70
1·590	67·59	1·730	79·80	1·829	91·90
1·595	68·05	1·735	80·24	1·830	92·10
1·600	68·51	1·740	80·68	1·831	92·30
1·605	68·97	1·745	81·12	1·832	92·52
1·610	69·43	1·750	81·56	1·833	92·75
1·615	69·89	1·755	82·00	1·834	93·05
1·620	70·32	1·760	82·44	1·835	93·43
1·625	70·74	1·765	82·88	1·836	93·80
1·630	71·16	1·770	83·32	1·837	94·20
1·635	71·57	1·775	83·90	1·838	94·60
1·640	71·99	1·780	84·50	1·839	95·00
1·645	72·40	1·785	85·10	1·840	95·60
1·650	72·87	1·790	85·70	1·8405	95·95
1·655	73·23	1·795	86·30	1·8410	97·00
1·660	73·64	1·800	86·90	1·8415	97·70
1·665	74·07	1·805	87·60	1·8410	98·20
1·670	74·51	1·810	88·30	1·8405	98·70
1·675	74·97	1·815	89·05	1·8400	99·20
1·680	75·42	1·820	90·05	1·8395	99·45
1·685	75·86	1·821	90·20	1·8390	99·70
1·690	76·30	1·822	90·40	1·8385	99·95
1·695	76·73				

HYDROCHLORIC ACID.

506. PERCENTAGE BY WEIGHT OF HCl PRESENT IN AQUEOUS SOLUTION OF KNOWN SPECIFIC GRAVITY AT 15·5° C., COMPARED WITH WATER AT 4° C. AND REDUCED TO VACUUM AS UNITY.

(Lunge and Marchlewski.)

Specific Gravity.	Percentage of Hydrochloric Acid.	Specific Gravity.	Percentage of Hydrochloric Acid.
1·000	0·16	1·105	20·97
1·005	1·15	1·110	21·92
1·010	2·14	1·115	22·86
1·015	3·12	1·120	23·82
1·020	4·13	1·125	24·78
1·025	5·15	1·130	25·75
1·030	6·15	1·135	26·70
1·035	7·15	1·140	27·66
1·040	8·16	1·145	28·61
1·045	9·16	1·150	29·57
1·050	10·17	1·155	30·55
1·055	11·18	1·160	31·52
1·060	12·19	1·165	32·49
1·065	13·19	1·170	33·46
1·070	14·17	1·175	34·42
1·075	15·16	1·180	35·39
1·080	16·15	1·185	36·31
1·085	17·13	1·190	37·23
1·090	18·11	1·195	38·16
1·095	19·06	1·200	39·11
1·100	20·01		

NITRIC ACID.

507. Percentage by Weight of HNO_3 present in Aqueous Solution of known Specific Gravity at 15·5° C., compared with Water at 4° C. and reduced to Vacuum as Unity.

(Lunge and Rey.)

Specific Gravity.	Percentage of HNO_3.	Specific Gravity.	Percentage of HNO .	Specific Gravity.	Percentage of HNO_3
1·000	0·10	1·175	28·63	1·350	55·79
1·005	1·00	1·180	29·38	1·355	56·66
1·010	1·90	1·185	30·13	1·360	57·57
1·015	2·80	1·190	30·88	1·365	58·48
1·020	3·70	1·195	31·62	1·370	59·39
1·025	4·60	1·200	32·36	1·375	60·30
1·030	5·50	1·205	33·09	1·380	61·27
1·035	6·38	1·210	33·82	1·385	62·24
1·040	7·26	1·215	34·55	1·390	63·23
1·045	8·13	1·220	35·28	1·395	64·25
1·050	8·99	1·225	36·03	1·400	65·30
1·055	9·84	1·230	36·78	1·405	66·40
1·060	10·68	1·235	37·53	1·410	67·50
1·065	11·51	1·240	38·29	1·415	68·63
1·070	12·33	1·245	39·05	1·420	69·80
1·075	13·15	1·250	39·82	1·425	70·98
1·080	13·95	1·255	40·58	1·430	72·17
1·085	14·74	1·260	41·34	1·435	73·39
1·090	15·33	1·265	42·10	1·440	74·68
1·095	16·32	1·270	42·87	1·445	75·98
1·100	17·11	1·275	43·64	1·450	77·28
1·105	17·89	1·280	44·41	1·455	78·60
1·110	18·67	1·285	45·18	1·460	79·98
1·115	19·45	1·290	45·95	1·465	81·42
1·120	20·23	1·295	46·72	1·470	82·90
1·125	21·00	1·300	47·49	1·475	84·45
1·130	21·77	1·305	48·26	1·480	86·05
1·135	22·54	1·310	49·07	1·485	87·70
1·140	23·31	1·315	49·89	1·490	89·60
1·145	24·08	1·320	50·71	1·495	91·60
1·150	24·84	1·325	51·53	1·500	94·09
1·155	25·60	1·330	52·37	1·505	96·39
1·160	26·36	1·335	53·22	1·510	98·10
1·165	27·12	1·340	54·07	1·515	99·07
1·170	27·88	1·345	54·93	1·520	99·67

POTASSIUM HYDRATE.

508. Percentage by Weight of KOH in Aqueous Solution of known Specific Gravity at 15·5° C.

(Lunge.)

Specific Gravity.	Percentage of KOH.	Specific Gravity.	Percentage of KOH.	Specific Gravity.	Percentage of KOH.
1·007	0·9	1·162	18·6	1·370	36·9
1·014	1·7	1·171	19·5	1·383	37·8
1·022	2·6	1·180	20·5	1·397	38·9
1·029	3·5	1·190	21·4	1·410	39·9
1·037	4·5	1·200	22·4	1·424	40·9
1·045	5·6	1·210	23·3	1·438	42·1
1·052	6·4	1·220	24·2	1·453	43·4
1·060	7·4	1·231	25·1	1·468	44·6
1·067	8·2	1·241	26·1	1·483	45·8
1·075	9·2	1·252	27·0	1·498	47·1
1·083	10·1	1·263	28·0	1·514	48·3
1·091	10·9	1·274	28·9	1·530	49·4
1·100	12·0	1·285	29·8	1·546	50·6
1·108	12·9	1·297	30·7	1·563	51·9
1·116	13·8	1·308	41·8	1·580	53·2
1·125	14·8	1·320	32·7	1·597	54·5
1·134	15·7	1·332	33·7	1·615	55·9
1·142	16·5	1·345	34·9	1·634	57·5
1·152	17·6	1·357	35·9		

SODIUM HYDRATE.

509. Percentage by Weight of NaOH in Aqueous Solution of known Specific Gravity at 15·5° C.

(Lunge.)

Specific Gravity.	Percentage of NaOH.	Specific Gravity.	Percentage of NaOH.	Specific Gravity.	Percentage of NaOH.
1·007	0·61	1·142	12·64	1·320	28·83
1·014	1·20	1·152	13·55	1·332	29·93
1·022	2·00	1·162	14·37	1·345	31·22
1·029	2·71	1·171	15·13	1·357	32·47
1·036	3·35	1·180	15·91	1·370	33·69
1·045	4·00	1·190	16·77	1·383	34·96
1·052	4·64	1·200	17·67	1·397	36·25
1·060	5·29	1·210	18·58	1·410	37·47
1·067	5·87	1·220	19·58	1·424	38·80
1·075	6·55	1·231	20·59	1·438	39·99
1·083	7·31	1·241	21·42	1·453	41·41
1·091	8·00	1·252	22·64	1·468	42·83
1·100	8·68	1·263	23·37	1·483	44·38
1·108	9·42	1·274	24·81	1·498	46·15
1·116	10·06	1·285	25·80	1·514	47·60
1·125	10·97	1·297	26·83	1·530	49·02
1·134	11·84	1·308	27·80		

AMMONIA.

510. Percentage by Weight of NH_3 in Aqueous Solution of known Specific Gravity at 15·5° C.

(Lunge and Wiernik.)

Specific Gravity.	Percentage of NH_3.	Specific Gravity.	Percentage of NH_3.	Specific Gravity.	Percentage of NH_3.
1·000	0·00	0·960	9·91	0·920	21·75
0·998	0·45	0·958	10·47	0·918	22·39
0·996	0·91	0·956	11·03	0·916	23·03
0·994	1·37	0·954	11·60	0·914	23·68
0·992	1·84	0·952	12·17	0·912	24·33
0·990	2·31	0·950	12·74	0·910	24·99
0·988	2·80	0·048	13·31	0·908	25·60
0·986	3·30	0·946	13·88	0·906	26·31
0·984	3·80	0·944	14·46	0·904	26·98
0·982	4·30	0·942	15·04	0·902	27·65
0·980	4·80	0·940	15·63	0·900	28·33
0·978	5·30	0·938	16·22	0·898	29·01
0·976	5·80	0·936	16·82	0·896	29·69
0·974	6·30	0·934	17·42	0 894	30 37
0·972	6·80	0·932	18·03	0·892	31·05
0·970	7·31	0·930	18·64	0·890	31·75
0·968	7·82	0·928	19·25	0·888	32·50
0·966	8·33	0·926	19·87	0·886	33·25
0·964	8·84	0·924	20·49	0·884	34·10
0·962	9·35	0·922	21·12	0·882	34·95

511. USEFUL MEMORANDA AND CONVERSION FACTORS

Weight of 1 c.c. of dry hydrogen at 0° C. and 760 mm. = 0·0000899 gm.
Weight of 1 c.c. of dry nitrogen at 0° C. and 760 mm. = 0·001257 gm.
Weight of 1 c.c. of dry air at 0° C. and 760 mm. = 0·001293 gm.
1 gm. molecule of a gas at 0° C. and 760 mm. measures 22·24 litres.
Weight of 1 c.c. of mercury at 0° C. = 13·596 gm.
Coefficient of expansion for gases = $\frac{1}{273}$ = 0·003665.
1 gallon = 4·54 litres.
1 litre = 1·76 pints.
1 oz. = 28·35 gm.
1 gm. = 15·4 grains.
1 cm. = 0·3937 inches.
1 inch = 2·54 cm.

512. Logarithms.

	0	1	2	3	4	5	6	7	8	9	Proportional Parts. 1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

512. Logarithms—*continued.*

	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	5	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

513. Anti-logarithms.

	0	1	2	3	4	5	6	7	8	9	Proportional Parts. 1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1 77	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	165 2	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

513. Anti-logarithms—*continued.*

	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

514. SPECIAL REAGENTS USED IN ORGANIC ANALYSES

Ammoniacal Silver Nitrate.—This is prepared by the addition of 10 per cent. ammonium hydroxide solution, drop by drop, to a 10 per cent. solution of silver nitrate, until the precipitate of silver hydroxide is just redissolved. See also "Tollen's Reagent," below.

Decolourised Magenta Solution (Schiff's Reagent).—Dissolve 0·2 gm. of rosaniline in 10 c.c. of freshly prepared, saturated sulphurous acid solution. Allow to stand until colourless. Dilute to 200 c.c. with distilled water, and keep in a well-stoppered bottle.

Erdmann's Reagent.—This is prepared by mixing 6 drops of pure HNO_3 with 100 c.c. of water; 12 drops of this solution are then mixed with 24 c.c. of pure conc. sulphuric acid.

De Vry's Reagent (Phosphomolybdic Acid).—Completely precipitate a solution of ammonium molybdate with an excess of sodium phosphate at 40–50° C. Leave for twenty-four hours, filter and wash the precipitate with water and dissolve it in a minimum amount of sodium carbonate solution. Evaporate and ignite until all the ammonia is driven off. Dissolve the residue in hot water, and add sufficient nitric acid to dissolve the precipitate first formed.

Fehling's Solution.—This is an alkaline solution of copper hydroxide, to which tartaric acid has been added to prevent the precipitation of the copper. It is prepared as described on page 318.

Froehde's Reagent is made by dissolving 1 gm. of ammonium molybdate in 100 gm. of pure conc. sulphuric acid.

Mandelin's Reagent is made by the solution of 1 gm. of vanadium chloride in 200 c.c. of pure conc. sulphuric acid.

Mayer's Reagent is made by dissolving 13·5 parts of mercuric chloride and 50 parts of potassium iodide in 940 parts of water.

Millon's Reagent.—To some mercury add twice its weight of pure nitric acid ($\Delta = 1{\cdot}42$). Gently warm until dissolved. Add two volumes of water, stand for six hours, and decant the clear solution of the reagent from the crystalline precipitate.

Sodium Bisulphite Solution.—This solution consists of a completely saturated solution of $NaHSO_3$ and should stand in the bottle with an excess of the solid reagent.

Tannic Acid is used in the form of a 10 per cent. aqueous solution.

Tollen's Reagent is a solution of ammoniacal silver nitrate containing free caustic soda. It is a much more delicate reagent than ordinary ammoniacal silver nitrate, and is prepared by mixing, *when required*, equal quantities of the following solutions :—

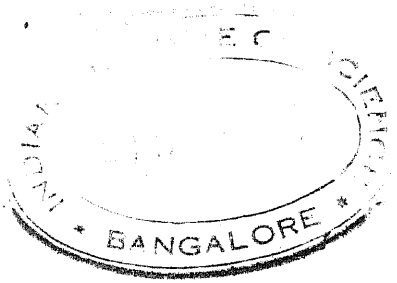
(i.) An aqueous 10 per cent. solution of caustic soda.

(ii.) Ammoniacal silver nitrate solution obtained by dissolving sufficient silver nitrate to yield a 10 per cent. solution in a mixture of equal volumes of strong ammonia and distilled water.

Since this reagent yields a black precipitate on heating alone, it must only be used in the cold.

Wagner's Reagent is a solution of iodine in potassium iodide solution. It is prepared by dissolving 5 parts of potassium iodide and 2 parts of iodine in 100 parts of water.

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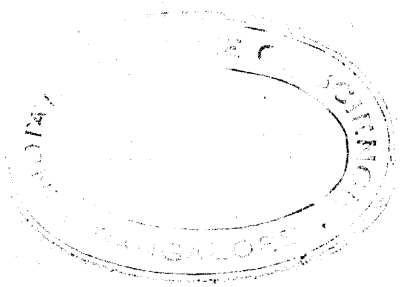
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